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THE RELATIVE MILLING AND BAKING QUALITY OF WESTERN CANADIAN SPRING WHEAT VARIETIES[1]

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Abstract

To maintain the quality of Canada's export wheat it is essential that only high quality varieties should be grown. To supply information on which a choice of varieties may be based, a co-operative study was made of the milling and baking quality of 25 varieties of spring wheat now grown in western Canada. Samples were grown in adjacent plots by the Dominion Experimental Farms and Universities in Manitoba, Saskatchewan and Alberta in 1928, 1929 and 1930. Only samples which were sound enough to be placed in the statutory grades by official inspectors were used. Part of each sample was milled and baked in each of the three co-operating laboratories. Four baking formulas were used. The varieties were classified on the bases of loaf volume, texture, crumb color, general appearance of loaf, absorption, and yield of straight flour. These classifications were combined to give classifications for baking quality and milling quality and finally for suitability for export and domestic milling. The last classification is given in Table XXVII and is, briefly, as follows:

1. Varieties which are entirely satisfactory: Reward, Ceres, Marquis, Pioneer, Red Fife, Renfrew, Red Bobs 222, Supreme.
2. Varieties which are fairly satisfactory: Early Red Fife, Ruby, Early Triumph.
3. Varieties which are unsatisfactory: (a) White wheats: Quality, Axminster, Hard Federation; (b) Varieties differing from Marquis in milling characteristics: Garnet, Kota; (c) Varieties inferior to Marquis in baking characteristics: Garnet, Parker's Selection, Brownhead, Huron, Kitchener, Preston, Marquillo.
4. Varieties which are very unsatisfactory: Early Prolific, Dicklow, Vermilion.

Introduction

The high reputation for quality of Canadian wheat was established when the major part of the production in western Canada was limited to one variety, Red Fife, grown in a comparatively small area. The extension of

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wheat growing westward and northward was favored by the introduction of an earlier-maturing variety, Marquis, which fully sustained the reputation established by Red Fife.

In recent years the enormous losses occasioned by plant diseases, insect pests, and drought, together with the spread of the wheat-growing area northward into regions where early frosts are a yearly menace, led to the development and introduction of new varieties in an effort to overcome these difficulties.

Many of the newer varieties differ from Marquis in shape, size and color of kernel and as a result there was a decrease in the uniformity of appearance of our export wheat. Uniformity is an important factor in the eyes of the buyers and varietal mixing has been the basis of complaints with regard to the quality of export shipments. This has naturally led to the question as to whether the new introductions are equal to Marquis in milling and baking quality. The present investigation was undertaken to obtain an answer to this question and to give a basis for the elimination of inferior varieties.

This paper deals with the quality of an extended series of varieties grown in 1928, 1929 and 1930.

Materials and Methods

Collection of Samples

In order that valid comparisons may be made between varieties it is essential that the samples compared should be grown under identical environmental conditions. It is a well-known fact that weather and soil conditions exert a profound influence on the chemical composition, and milling and baking quality of wheat. The variation in quality in samples of a single variety grown at different places is so great that varieties to be compared must be grown in adjacent plots. Furthermore, since the varieties in a series of samples grown in different places will not always fall in the same order with respect to quality it is unsafe to draw conclusions from the results of a single series. Finally a sound sample of one variety should not be compared with a damaged sample of another variety.

For this study samples were obtained from adjacent plots of the varieties under test grown at the Universities and Experimental Farms in the three prairie provinces in the years 1928 to 1930 inclusive. These samples were graded by inspectors of the Western Grain Inspection Division and only samples which graded into the statutory grades were used in our comparisons.

Co-operating Stations

University of Alberta, University of Manitoba, University of Saskatchewan, and the Dominion Experimental Farms at Beaverlodge, Brandon, Fort Vermilion, Indian Head, Lacombe, Lethbridge, Morden, Rosthern and Scott.

Varieties Tested

Axminster, Brownhead, Ceres, Dicklow, Early Prolific, Early Red Fife, Early Triumph, Garnet, Hard Federation, Huron, Kitchener, Kota, Marquillo, Marquis, Parker's Selection, Pioneer, Preston, Quality, Red Bobs 222, Red Fife, Renfrew, Reward, Ruby, Supreme, Vermilion.

Criteria of Quality

A wheat of good quality is one which will produce a high yield of flour of good baking quality. This definition is far from precise. Although the possible yield of flour from any wheat is the main factor in milling quality, the miller also considers the tempering properties, the capacity to blend well with other wheats and the power required in milling. Baking quality is a relative term and there is no absolute measure of this important characteristic. One has to consider the suitability of a flour for large machine bakeries, small hand bakeries, home baking, straight dough and sponge dough systems, long and short fermentations, and the particular type of loaf desired in any given locality. However the quality of a sound sample of Marquis wheat grown under favorable climatic and soil conditions is universally accepted as the standard of quality for Canadian wheat. This gives a standard of comparison which is independent of local conceptions of quality.

The milling quality of the varieties was determined by the yield of straight flour obtained in a milling test. The other factors in milling quality outlined above were not determined quantitatively but were the subject of general observation by the millers making the tests.

The baking quality was judged by the loaf volume, absorption, texture and color of crumb and the general appearance of the loaf, which includes the shape, and the color of the crust. Information on these points was obtained using four different formulas in the baking procedure. While it is true that the handling qualities and the stability and elasticity of the dough are important factors in baking quality it is exceedingly difficult to measure them or to express them numerically. The use of four baking formulas giving, in effect, a wide range of baking conditions, makes it extremely unlikely that inherent weakness in any of the varieties studied remained undiscovered.

In addition to using these primary criteria of quality, the varieties were compared on the basis of weight per measured bushel, which is universally used as an index of milling yield, and on the basis of the protein content of the wheat, which is regarded, on the American Continent, as a good general index of baking quality.

Methods

The samples received from the co-operating stations were cleaned at the collecting laboratory and then divided into three sub-samples which were distributed to the three co-operating laboratories. Our results are therefore based on the average of three independent tests.

The details of our methods of analysis and milling and baking tests have been given fully in several published papers (1, 3, 4) and it is unnecessary to repeat them here. It seems desirable, however, to indicate the nature of the four formulas used in the baking tests.

1. *Simple:* flour, yeast, salt, sugar and water. This formula gives information on the quality of the flour unaffected by the addition of "improvers". If used as the sole criterion of quality, however, it may lead to entirely erroneous comparisons. Flours with a high protein content which are deficient in gas production seldom show their maximum capabilities with this formula.

2. *Bromate:* simple formula plus potassium bromate. The action of the potassium bromate is as yet obscure but it is known that it directly or indirectly affects the protein. It is the basis of some improvers in wide commercial use. This formula appears to be particularly adapted for the estimation of quality of high protein Canadian wheat.

3a. *Malt:* simple formula plus non-diastatic malt. This formula was used with the 1928 samples.

3b. *Malt-phosphate:* simple formula plus small percentages of diastatic malt and ammonium phosphate. This formula was used with the 1929 and 1930 samples.

Both of these formulas are designed to insure an adequate supply of gas for raising the dough. Flours with a high percentage of protein of good quality but which are deficient in gas production will show to advantage when baked by these formulas.

4. *Blend-bromate:* flour blended with 50% soft wheat flour and then baked by the bromate formula. Baking tests using this formula give information on the ability of the test flour to "carry" a weaker flour. This is important since the bulk of our wheat is sold for export and is blended either before or after milling.

Analysis of Results

Introductory Discussion

The restriction of the samples to grade Four Northern or better seriously cut down the number of available samples in 1928 owing to the number of frosted samples and to a lesser extent in the other years. Also, for various reasons, the entire series of samples was not grown at all stations in all three years. It was therefore impossible to compare all the varieties by a single statistical analysis. Hence, it was necessary to split the series into overlapping groups in which valid comparisons could be obtained, analyzing the results for each group separately. These were then combined by reference to the results for varieties which were common to a number of these groups. By using this method varieties were compared directly only when they had been grown under identical conditions. Once the relative quality of the varieties for each group has been determined in this manner the combination into one classification containing all the varieties studied is valid, provided that the order of the varieties and not the numerical results is considered.

The results in each group were analyzed by the application of Fisher's analysis of variance (2).

In the analysis of variance the total variability of an experiment is expressed as a sum of squares of the deviations of each individual determination from the general mean. This sum of squares is then divided up into component parts and each of these sums of squares may be used to estimate the variability of the experiment by calculating for it a variance (which is the sum of squares divided by the corresponding number of degrees of freedom). The differences between these estimates of the variance bring out the important factors in the experiment and their significance can be measured by means of the Z test.

For any two estimates of the variance the Z value is one-half the difference between their natural logarithms. If the Z value obtained equals or exceeds the corresponding Z value at the 5% (or 1%) point, it may be said that the observed difference between the estimates of variance would occur, by chance, in only 5% (or 1%) of the cases in a large number of trials.

This method of analysis made it possible to study the differences between varieties, entirely separate from the variation in one variety grown at different places or baked by different formulas. Further, it was possible to get an accurate measure of the effect of different growing conditions, occasioned by the samples being grown in different places and different years, on the constancy of the order in which the varieties fall with respect to any particular character. The method has also the advantage that it gives an accurate estimate of the error of the experiment and hence of the significance of the differences found. A difference of more than three times the standard error is considered to be significant. In making the classification for any given character, Marquis was used as the standard. Varieties falling above (or below) this standard were regarded as superior (or inferior) in that particular character. Varieties falling below Marquis may be adapted to special uses, but from the standpoint of the quality desired in our export wheat they must definitely be regarded as inferior.

Analysis of Baking Data

In analyzing the results of the baking tests each of the five baking characteristics was studied separately. When the restrictions in regard to year and place of growth and soundness of samples, discussed in the foregoing section, were imposed upon the comparison of varieties, these fell into thirteen groups, all containing the varieties Early Triumph, Huron, Marquis, Red Bobs 222 and Reward. The data for each group were subjected to an analysis of variance, an example of which is given in Table I. It will be seen that no attempt was made to study the variation between years or between places.

TABLE I

Analysis of variance

Loaf volume

	Sum of squares loaf volume	Degrees of freedom	Variance	$\frac{1}{2}\,\mathrm{Log}_e$	Z
Series (S)	4606.87	13	354.37	2.9352	1.8382
Varieties (V)	2332.77	4	583.19	3.1842	2.0872
Formulas (F)	10799.04	3	3599.68	4.0943	2.9973
V × F	815.17	12	67.93	2.1092	1.0122
F × S	2381.16	39	61.05	2.0559	0.9589
V × S	1171.63	52	22.53	1.5574	0.4604
Error	1399.63	156	8.97	1.0970	—

Varieties:– Reward, Marquis, Red Bobs 222, Early Triumph, Huron.
Series:– Lacombe 1930, Edmonton 1929 and 1930, Beaverlodge 1930, Saskatoon 1929 and 1930, Scott 1929 and 1930, Swift Current 1930, Indian Head 1930, Rosthern 1929 and 1930, Winnipeg 1929, Brandon 1929.

Each series was regarded as having been grown under different environmental conditions even though in many cases series were grown in the same place but in different years.

In studying the relative qualities of the varieties the important portions of the variance are:

1. Variance between varieties. By comparing this with the variance due to error the significance of the differences between varieties can be estimated.

2. Interaction of varieties and series (V × S). This gives a measure of the constancy of the order of the varieties when grown under different environments.

3. Interaction of varieties and formulas (V × F). This gives a measure of the constancy of the order of the varieties when baked by different formulas.

4. Variance due to error. This represents the portion of the total variance which cannot be satisfactorily accounted for by known causes of variation. It is used in estimating the significance of the other portions of the variance and also in estimating the significance of the differences between the varieties by means of the standard error which is calculated from it.

Analyses of variance for loaf volume similar to that shown in Table I were made for each of the 13 groups previously mentioned. The results are summarized in Table II in terms of the ratio of the Z value obtained to the Z value at the corresponding 5% point, ratios of 1.0 or greater being significant.

When the varieties in each group are arranged in relative order a compilation such as that in Table IV for loaf volume is obtained. It will be observed that the absolute values for any given variety vary from group to group, owing to the fact that these groups represent different combinations of varieties, stations, and years. The minimum significant differences were used as units for placing the varieties in classes with respect to Marquis as a standard. This placing is given for loaf volume in Table V. The procedure may be more easily followed in a specific example. In Table IV (Group 1) the varieties fall in the order Reward, Marquis, Red Bobs 222, Early Triumph and Huron. The significant difference between varieties is 12 cc. The average volumes of these varieties are 666, 628, 616, 600 and 580 respectively. It will be seen that the difference between Reward and Marquis is between 3 and 4 times the significant difference and Reward was accordingly placed in class +3 in Table V. Similarly, Red Bobs 222 which is just significantly different from Marquis is placed in class −1, Early Triumph in class −2 and Huron in class −4. All the other groups in the table were treated in a similar manner and the same procedure was followed in subsequent tabulations of other characters. These classifications together with the information in the tables of averages were used as the bases for single classifications for each characteristic.

Loaf Volume

Turning now to a more detailed consideration of the data for loaf volume it will be noted from Table II that all the components of variance are significant. The differences between varieties are much greater than could have occurred merely by chance. The interaction between variety and formula is highly

significant. This means that the formula used has a pronounced influence on the order in which the varieties fall with respect to loaf volume. While the averages of all formulas have been used in the classifications, important differences in the results of the four formulas will be noted in the description of the individual varieties. The interactions between variety and series are also statistically significant. That is to say, the order of the varieties with respect to loaf volume will vary when the varieties are grown at different places or in different years. It should be pointed out, however, that the level of significance is, in this case, comparatively low and that in practice the variation

TABLE II

SIGNIFICANCE OF COMPONENTS OF VARIANCE
LOAF VOLUME

Group	Number of series	Ratio of Z obtained to Z at 5% point					
		Series (S)	Varieties (V)	Formulas (F)	Interactions		
					V × F	F × S	V × S
1	14	6.4	4.7	6.1	3.4	4.9	2.6
2	11	4.8	5.1	6.3	3.9	4.5	2.3
3	11	6.2	5.2	6.2	3.5	5.3	2.7
4	8	3.2	5.5	5.5	3.8	2.9	2.3
5	12	5.8	4.7	6.0	3.8	5.1	2.5
6	10	5.4	4.5	5.9	4.0	4.3	2.5
7	13	5.7	4.4	6.0	4.1	4.0	2.4
8	10	4.2	4.7	6.3	3.7	4.3	1.5
9	11	5.9	4.7	6.2	3.5	5.4	3.0
10	7	4.2	4.2	5.6	2.5	4.4	1.3
11	5	1.7	4.6	5.0	3.3	1.3	0.0
12	6	4.8	3.8	5.7	3.2	3.7	1.9
13	6	4.6	4.0	5.9	3.9	3.5	2.6

in order from series to series is not sufficient to invalidate our general conclusions. In Table IV (Group 1) it will be seen that the average loaf volumes fall in the order Reward, Marquis, Red Bobs 222, Early Triumph and Huron. The position of each of these varieties for each station and each year entering into the analysis was determined and the frequency with which each variety fell in each of the five positions is shown in Table III.

TABLE III

FREQUENCY OF POSITION IN 14 SERIES OF COMPARISONS OF LOAF VOLUME (AVERAGE) FOR REWARD, MARQUIS, RED BOBS 222, EARLY TRIUMPH AND HURON

	1st	2nd	3rd	4th	5th
Reward	12	2	0	0	0
Marquis	2	7	2	3	0
Red Bobs 222	0	3	10	1	0
Early Triumph	0	1	2	9	2
Huron	0	1	0	1	12

TABLE IV

AVERAGE LOAF VOLUME OF EACH VARIETY IN EACH GROUP

Loaf volume, cc.	Group 1	2	3	4	5	6	7	8	9	10	11	12	13
	Minimum significant difference (cc.)												
	12	14	16	17	14	15	14	13	14	15	25	17	17
680–689		Reward									Reward		
670–679			Kota	Reward			Reward	Reward					
660–669	Reward					Reward				Reward		Reward	Reward
650–659			Reward		Reward				Reward Ceres		Marquis		
640–649				Marquis				Marquis					
630–639		Marquis Red Fife				Marquis	Marquis						
620–629	Marquis	Red Bobs 222 Renfrew	Axminster Marquis	Red Bobs 222				Red Bobs 222 Early R. Fife	Marquis	Marquis	Red Bobs 222	Marquis	Marquis
610–619	Red Bobs 222		Marquillo Parker's Sel.		Marquis	Red Bobs 222	Red Bobs 222 Supreme			Red Bobs 222	E. Triumph	Red Bobs 222 E. Triumph	E. Triumph
600–609	E. Triumph	E. Triumph	Red Bobs 222 Preston	E. Triumph	Red Bobs 222 E. Triumph	E. Triumph	E. Triumph	E. Triumph	Red Bobs 222 Quality E. Triumph	Ruby E. Triumph			Red Bobs 222
590–599		Kitchener Huron	E. Triumph	Huron							Huron		Brownhead
580–589	Huron		Huron			Huron Hard Fed'tion	Huron	Huron				Huron	Huron Early Prolific
570–579					Garnet				Huron				
560–569					Huron					Huron			
550–559													
540–549													
530–539													
520–529													
510–519				Dicklow									
500–509										Vermilion			

TABLE V

Classification on basis of minimum significant difference from Marquis

Loaf volume

Class	Group												
	1	2	3	4	5	6	7	8	9	10	11	12	13
	Minimum significant difference (cc.)												
	12	14	16	17	14	15	14	13	14	15	25	17	17
+3	Reward	Reward	Kota		Reward								
+2			Reward			Reward	Reward	Reward	Reward Ceres	Reward			Reward
+1				Reward							Reward	Reward Pioneer	
0	Marquis	Marquis Red Fife Red Bobs 222	Axminster Marquis Marquillo Parker's Sel. Red Bobs 222	Marquis	Marquis Red Bobs 222	Marquis	Marquis Red Bobs 222	Marquis	Marquis	Marquis Red Bobs 222	Marquis	Marquis Red Bobs 222 E. Triumph	Marquis E. Triumph Red Bobs 222
−1	Red Bobs 222	Renfrew	Preston E. Triumph	Red Bobs 222	E. Triumph	Red Bobs 222 E. Triumph	Supreme E. Triumph	Early R. Fife Red Bobs 222	Red Bobs 222 Quality E. Triumph	E. Triumph Ruby	Red Bobs 222 E. Triumph		
−2	E. Triumph	E. Triumph Kitchener	Huron	E. Triumph	Garnet	Huron		E. Triumph			Huron	Huron	Brownhead Huron Early Prolific
−3		Huron		Huron	Huron	Hard Fed'tion	Huron		Huron	Huron			
−4	Huron							Huron					
−5												Vermilion	
−6													
−7				Dicklow									

TABLE VI

CLASSIFICATION OF VARIETIES ON BASIS OF LOAF VOLUME

1. *Superior to Marquis*
   Kota
   Reward
   Ceres
   Pioneer

2. *Equal to Marquis*
   Axminster
   Marquis
   Marquillo
   Red Fife, Parker's Selection

3. *Slightly inferior to Marquis*
   Red Bobs 222
   Supreme, Early Red Fife
   Renfrew
   Preston, Quality
   Early Triumph, Ruby

4. *Decidedly inferior to Marquis*
   Kitchener, Brownhead
   Garnet
   Huron, Early Prolific
   Hard Federation

5. *Very much inferior to Marquis*
   Vermilion
   Dicklow

It will be seen that there is some variation in position but there is little doubt that the general conclusion that the varieties fall in the order previously named is correct. A similar argument can be applied to the other varieties.

The information contained in Table IV was brought to a common basis by the method previously outlined and the results are given in Table V.

From Table V the single classification in Table VI was compiled. The order of the varieties in each class is that arrived at from the data, but the differences between the varieties within any one class probably have no practical significance. However, in the further combinations of the classifications it is useful to know whether the variety fell near the top or the bottom of any class.

Texture

Table VII shows significant differences in the texture of varieties and significant interaction between variety and formula. The interaction between variety and series is less significant than in the case of loaf

TABLE VII

SIGNIFICANCE OF COMPONENTS OF VARIANCE
TEXTURE

Group	Number of series	Ratio of Z obtained to Z at 5% point					
		Series (S)	Varieties (V)	Formulas (F)	Interactions		
					V × F	F × S	V × S
1	14	4.2	2.7	5.7	2.0	4.7	0.9
2	11	4.3	2.9	5.9	1.8	4.0	0.7
3	11	5.4	2.6	6.1	2.8	6.3	1.8
4	8	3.9	3.4	5.6	1.5	3.7	0.6
5	12	3.5	2.9	5.5	2.1	4.6	1.7
6	10	4.4	2.4	5.5	1.8	5.2	0.5
7	13	4.1	3.5	5.8	3.0	5.5	2.5
8	10	3.7	2.4	5.7	2.5	3.9	1.0
9	11	3.4	2.0	5.5	2.1	4.8	0.8
10	7	3.4	2.3	5.4	1.9	3.6	1.5
11	5	2.6	3.6	3.8	1.5	2.0	0.0
12	6	3.3	1.6	4.5	1.4	3.7	0.5
13	6	3.3	3.2	4.6	1.9	3.6	0.0

TABLE VIII

AVERAGE TEXTURE SCORE OF EACH VARIETY IN EACH GROUP

Texture score	Group 1	2	3	4	5	6	7	8	9	10	11	12	13
	Minimum significant difference												
	0.28	0.30	0.28	0.35	0.28	0.28	0.25	0.29	0.30	0.32	0.50	0.37	0.37
7.5													
7.4		Renfrew					Supreme			Marquis			
7.3			Reward		Reward				Reward Marquis		Marquis	Marquis	Reward
7.2	Reward	Reward			Marquis	Hard Fed'tion Reward	Reward	Marquis Reward			Reward	Reward	Marquis
7.1	Marquis	Kitchener Marquis		Reward			Marquis		Ceres	Reward Ruby		Pioneer	
7.0			Marquis Axminster	Marquis		Marquis			Red Bobs 222		E. Triumph Red Bobs 222		E. Triumph Red Bobs 222 Brownhead
6.9			Kota E. Triumph Red Bobs 222		Red Bobs 222 E. Triumph			Early R. Fife	Quality E. Triumph	Red Bobs 222 E. Triumph		Red Bobs 222	
6.8	Red Bobs 222 E. Triumph	Red Bobs 222	Preston			E. Triumph	Red Bobs 222	Red Bobs 222 E. Triumph			Huron	E. Triumph	Huron
6.7		E. Triumph Red Fife	Parker's Sel.			Red Bobs 222	E. Triumph		Huron			Huron	
6.6		Huron	Huron	E. Triumph Huron	Garnet	Huron		Huron		Huron			
6.5	Huron		Marquillo		Huron		Huron						
6.4													
6.1													
6.0													
5.9													Early Prolific
5.8				Dicklow									
5.2											Vermilion		

TABLE IX

Classification on basis of minimum significant difference

Texture

Class	Group												
	1	2	3	4	5	6	7	8	9	10	11	12	13
	Minimum significant difference												
	0.28	0.30	0.28	0.35	0.28	0.28	0.25	0.29	0.30	0.32	0.50	0.37	0.37
+1		Renfrew	Reward				Supreme						
0	Reward Marquis	Reward Marquis Kitchener	Marquis Axminster Kota Red Bobs 222 E. Triumph Preston	Reward Marquis Red Bobs 222	Reward Marquis	Hard Fed'tion Reward Marquis E. Triumph	Reward Marquis	Reward Marquis	Reward Marquis Ceres	Marquis Reward Ruby	Marquis Reward E. Triumph Red Bobs 222	Marquis Reward Pioneer	Reward Marquis E. Triumph Red Bobs 222 Brownhead
−1	Red Bobs 222 E. Triumph	Red Bobs 222 E. Triumph Red Fife Huron	Parker's Sel. Huron Marquillo	E. Triumph Huron	Red Bobs 222 E. Triumph	Red Bobs 222	Red Bobs 222 E. Triumph	Early R. Fife Red Bobs 222 E. Triumph	Red Bobs 222 Quality E. Triumph	Red Bobs 222 E. Triumph Huron	Huron	Red Bobs 222 E. Triumph Huron	Huron
−2	Huron				Garnet Huron		Huron	Huron	Huron				
−3				Dicklow									Early Prolific
−4											Vermilion		

volume. This means that the order of the varieties with respect to texture is less affected by environmental conditions than was the order with respect to loaf volume, and hence that the conclusions with regard to this characteristic will have general validity. The actual values for the averages of each group are given in Table VIII and the adjusted classification in Table IX.

These group classifications were combined on the same basis as those for loaf volume to give the single classification in Table X.

TABLE X

CLASSIFICATION OF VARIETIES ON BASIS OF TEXTURE

1.	*Superior to Marquis*
	Renfrew, Supreme
2.	*Equal to Marquis*
	Hard Federation
	Reward
	Marquis, Kitchener
	Axminster
	Pioneer
	Ceres, Kota, Ruby
3.	*Slightly inferior to Marquis*
	Early Red Fife
	Red Bobs 222
	Brownhead, Preston
	Red Fife, Quality, Early Triumph
	Parker's Selection
	Garnet
	Huron
	Marquillo
5.	*Very much inferior to Marquis*
	Dicklow, Early Prolific
	Vermilion

Crumb Color

Table XI shows the difference between varieties to be significant. The interactions between variety and formula and between variety and series are low and in some of the groups are not significant. This is to be expected since the pigmentation of the flour and hence of the bread is a definite varietal characteristic. The classifications for the various groups on the basis of the actual values are given in Table XII and on the adjusted basis in Table XIII.

TABLE XI

SIGNIFICANCE OF COMPONENTS OF VARIANCE

COLOR

Group	Number of series	Ratio of Z obtained to Z at 5% point					
		Series (S)	Varieties (V)	Formulas (F)	Interactions		
					V × F	F × S	V × S
1	14	3.8	3.3	5.3	0.9	3.8	0.0
2	11	4.1	2.9	5.6	0.7	3.7	1.9
3	11	5.0	4.3	5.7	1.2	4.2	0.0
4	8	0.8	4.4	4.8	0.8	1.8	3.5
5	12	3.4	4.0	5.2	1.2	3.6	0.2
6	10	3.3	3.3	4.8	1.4	3.1	0.0
7	13	3.8	3.4	5.3	2.3	3.8	1.1
8	10	3.5	2.7	5.2	0.7	2.7	0.0
9	11	4.0	3.5	5.3	0.7	4.3	0.8
10	7	3.2	2.8	5.2	0.4	3.5	0.7
11	5	2.3	3.3	3.9	0.4	0.0	0.0
12	6	3.0	2.5	4.4	0.0	2.6	0.0
13	6	3.5	3.8	4.5	0.6	2.3	0.0

TABLE XII

AVERAGE CRUMB COLOR SCORE FOR EACH VARIETY IN EACH GROUP

Crumb color score	Group												
	1	2	3	4	5	6	7	8	9	10	11	12	13
	Minimum significant difference												
	0.28	0.32	0.29	0.50	0.29	0.33	0.28	0.34	0.29	0.37	0.45	0.41	0.36
7.9											Marquis		
7.8											Reward		Marquis Reward
7.7									Marquis	Marquis		Marquis	
7.6	Marquis	Marquis	Marquis		Reward Marquis	Marquis	Marquis Supreme	Marquis	Reward	Reward		Reward	
7.5	Reward	Reward		Marquis		Hard Fed'tion	Reward	Reward	Quality Ceres		Red Bobs 222		
7.4		Renfrew	Reward										Red Bobs 222
7.3		Red Fife				Reward			Red Bobs 222				
7.2		Red Bobs 222	Red Bobs 222	Reward	Red Bobs 222 E. Triumph			Early R. Fife Red Bobs 222		Red Bobs 222 E. Triumph	E. Triumph	Red Bobs 222 E. Triumph	E. Triumph
7.1	Red Bobs 222 E. Triumph	E. Triumph				Red Bobs 222	Red Bobs 222 E. Triumph	E. Triumph	E. Triumph	Ruby		Pioneer	
7.0			E. Triumph	Red Bobs 222 E. Triumph		E. Triumph					Huron		Brownhead
6.9		Kitchener											
6.8			Kota										Huron
6.7		Huron	Huron Axminster			Huron		Huron	Huron	Huron			
6.6	Huron		Preston	Huron	Huron		Huron					Huron	
6.5			Marquillo Parker's Sel.										
6.4					Garnet								
6.3													Early Prolific
6.2											Vermilion		
4.7				Dicklow									

TABLE XIII

CLASSIFICATION ON BASIS OF MINIMUM SIGNIFICANT DIFFERENCE
CRUMB COLOR

Class	Group												
	1	2	3	4	5	6	7	8	9	10	11	12	13
	Minimum significant difference												
	0.28	0.32	0.29	0.50	0.29	0.33	0.28	0.34	0.29	0.37	0.45	0.41	0.36
0	Marquis Reward Red Bobs 222 E. Triumph	Marquis Reward Renfrew Red Fife	Marquis Reward	Marquis Reward	Reward Marquis	Marquis Hard Fed'tion Reward	Marquis Supreme Reward	Marquis Reward	Marquis Reward Quality Ceres	Marquis Reward	Marquis Reward Red Bobs 222	Marquis Reward	Marquis Reward
−1		Red Bobs 222 E. Triumph	Red Bobs 222	Red Bobs 222 E. Triumph Huron	Red Bobs 222 E. Triumph	Red Bobs 222 E. Triumph	Red Bobs 222 E. Triumph	Early R. Fife Red Bobs 222 E. Triumph	Red Bobs 222	Red Bobs 222 E. Triumph Ruby	E. Triumph	Red Bobs 222 E. Triumph Pioneer	Red Bobs 222 E. Triumph
−2		Kitchener Huron	E. Triumph Kota		Huron	Huron		Huron	E. Triumph	Huron	Huron	Huron	Brownhead Huron
−3	Huron		Axminster Huron Preston Marquillo Parker's Sel.				Huron		Huron		Vermilion		
−4					Garnet								Early Prolific
−5				Dicklow									

TABLE XIV

CLASSIFICATION OF VARIETIES ON BASIS OF CRUMB COLOR

2.	*Equal to Marquis*
	Marquis, Hard Federation, Supreme
	Reward
	Renfrew, Quality, Ceres
	Red Fife
3.	*Slightly inferior to Marquis*
	Early Red Fife
	Red Bobs 222
	Early Triumph
	Ruby
	Pioneer
4.	*Decidedly inferior to Marquis*
	Kitchener
	Kota, Brownhead, Axminster
	Huron
	Preston
	Marquillo
	Parker's Selection
	Garnet
5.	*Very much inferior to Marquis*
	Vermilion, Early Prolific
	Dicklow

The combination of the individual classifications was made on the same basis as before, and is given in Table XIV.

General Appearance

The score for general appearance is the sum of the scores for shape of loaf and color of crust. The analysis of variance gave similar results to those for texture. Table XV shows that the differences between varieties are significant and while the interactions, formula × variety and series × variety, are statistically significant they are unimportant practically. The classifications are given in Tables XVI and XVII.

The classifications by groups were combined in the same manner as for loaf volume and the combined classification is given in Table XVIII.

Absorption

The analysis of variance applied to this character differed from that applied to the others. The change was necessitated by the fact that in all laboratories the practice was followed of determining the correct absorption for each

TABLE XV

SIGNIFICANCE OF COMPONENTS OF VARIANCE
GENERAL APPEARANCE

Group	Number of series	Ratio of Z obtained to Z at 5% point					
		Series (S)	Varieties (V)	Formulas (F)	Interactions		
					V × F	F × S	V × S
1	14	3.9	2.6	3.3	1.7	4.8	1.2
2	11	3.4	3.1	3.6	2.4	4.1	0.6
3	11	3.9	2.4	3.3	1.3	5.1	1.4
4	8	2.7	4.0	3.1	2.1	2.8	0.2
5	12	3.8	2.1	2.6	1.8	4.4	1.3
6	10	3.0	1.9	3.3	1.0	3.3	1.2
7	13	3.2	2.4	3.1	1.7	4.4	1.3
8	10	4.7	3.8	4.3	3.7	6.0	4.7
9	11	3.6	2.8	3.6	1.8	5.4	0.9
10	7	3.5	2.6	2.4	1.7	4.4	0.3
11	5	2.3	4.4	2.9	3.0	1.7	0.0
12	6	2.4	1.6	2.8	1.1	2.3	0.7
13	6	2.7	3.0	3.5	1.2	2.4	1.6

TABLE XVI

AVERAGE GENERAL APPEARANCE SCORE FOR EACH VARIETY IN EACH GROUP

General appearance score	Group 1	2	3	4	5	6	7	8	9	10	11	12	13
	Minimum significant difference 0.25	0.29	0.30	0.38	0.29	0.31	0.29	0.18	0.28	0.33	0.43	0.38	0.37
8.9											Marquis		
8.8											Reward	Marquis	
8.7		Reward		Marquis				Marquis	Ceres				Marquis
8.6	Reward	Renfrew Marquis		Reward		Marquis		Reward		Marquis		Pioneer Reward Red Bobs 222	Reward
8.5	Marquis		Reward Axminster Kota		Reward	Reward	Reward Marquis Supreme	Early R. Fife	Reward Marquis	Ruby Reward	Red Bobs 222		Red Bobs 222
8.4		Red Bobs 222		Red Bobs 222	Marquis	Red Bobs 222		Red Bobs 222		Red Bobs 222	E. Triumph		E. Triumph
8.3	Red Bobs 222		Marquis Red Bobs 222 Parker's Sel.		Red Bobs 222		Red Bobs 222		Red Bobs 222			E. Triumph	
8.2		Red Fife	Preston		Garnet	Hard Fed'tion							Brownhead
8.1		Kitchener							E. Triumph Quality		Huron		Huron
8.0	Huron E. Triumph	Huron	Marquillo Huron	Huron	E. Triumph	E. Triumph Huron	E. Triumph Huron	E. Triumph Huron	Huron	E. Triumph		Huron	
7.9		E. Triumph	E. Triumph	E. Triumph	Huron								
7.8										Huron			
7.7													
7.6													
7.5													Early Prolific
6.9				Dicklow									
6.2											Vermilion		

TABLE XVII

Classification on basis of minimum significant difference

General appearance

Class	Group												
	1	2	3	4	5	6	7	8	9	10	11	12	13
	Minimum significant difference												
	0.25	0.30	0.30	0.38	0.29	0.31	0.29	0.18	0.28	0.33	0.43	0.38	0.37
0	Reward Marquis Red Bobs 222	Reward Marquis Renfrew Red Bobs 222	Axminster Kota Reward Red Bobs 222 Marquis Parker's Sel. Preston	Marquis Reward Red Bobs 222	Reward Marquis Red Bobs 222 Garnet	Marquis Reward Red Bobs 222	Marquis Reward Supreme Red Bobs 222	Marquis Reward	Ceres Reward Marquis Red Bobs 222	Marquis Reward Ruby Red Bobs 222	Marquis Reward	Marquis Reward Pioneer Red Bobs 222	Marquis Reward Red Bobs 222 E. Triumph
−1		Red Fife Kitchener	Huron Marquillo E. Triumph	Huron		Hard Fed'tion Huron E. Triumph	E. Triumph Huron	Early R. Fife Red Bobs 222	E. Triumph Quality Huron	E. Triumph	Red Bobs 222 E. Triumph	E. Triumph	Brownhead Huron
−2	E. Triumph Huron	Huron E. Triumph		E. Triumph	E. Triumph Huron					Huron	Huron	Huron	
−3								E. Triumph Huron					Early Prolific
−4				Dicklow									
−5													
−6											Vermilion		

TABLE XVIII

CLASSIFICATION OF VARIETIES ON BASIS OF GENERAL APPEARANCE

2. *Equal to Marquis*
Ceres
Reward, Kota, Axminster
Supreme
Marquis, Renfrew, Ruby
Parker's Selection, Pioneer, Preston, Garnet
Red Bobs 222
3. *Slightly inferior to Marquis*
Early Red Fife
Red Fife, Hard Federation
Kitchener
Huron, Marquillo
Early Triumph, Quality, Brownhead
5. *Very much inferior to Marquis*
Dicklow, Early Prolific
Vermilion

TABLE XIX

SIGNIFICANCE OF COMPONENTS OF VARIANCE ABSORPTION

Group	Number of series	Ratio of Z obtained to Z at 5% point	
		Varieties	Places
1	14	0.0	0.0
2	11	0.4	2.4
3	11	4.2	4.9
4	8	4.1	2.7
5	12	0.0	2.6
6	10	0.0	2.9
7	13	1.3	4.0
8	10	0.0	2.5
9	11	2.5	3.3
10	7	1.6	2.0
11	5	1.6	1.4
12	6	0.0	1.5
13	6	1.2	1.1

sample and then using the same amount of water for all subsequent bakings. The variance was therefore split into only three portions, between varieties, places and error. The results are given in Table XIX.

It will be seen that in only a few groups are the differences between varieties significant. In these experiments, only six varieties were significantly differentiated from Marquis. Kota, Ceres and Ruby had high absorption, Supreme and Brownhead were very slightly lower than Marquis, and Vermilion was decidedly low.

General Baking Quality

It is now necessary to combine the data for the individual characters into a single classification for baking quality. In the classifications given so far, once the basis was selected, the class into which each variety was placed was governed solely by the numerical data obtained. In combining these to give a classification for baking quality, however, the weight which should be given to each of the baking characteristics is a matter of opinion. It seems to us that loaf volume must be considered the most important factor because, while, in general, very large loaves are not demanded commercially, loaf volume is the most sensitive index of changes in the character of the flour and is the most susceptible of precise measurement. When the baking formula insures adequate gas production, it gives a good indication of strength, provided the flour was produced from sound wheat as in the samples here tested. It was therefore taken as the principal basis for the classification in respect to baking quality. Texture was ranked next in importance because varieties which give poor texture cannot be regarded as having good baking quality. In a study of varieties crumb color should be ranked high in importance. While loaf volume and texture are strongly influenced by environment, carotin content is essentially an inherent varietal characteristic. Although

yellow color in flour can be bleached quite readily, good color is desirable since bleaching is prohibited in some countries, adds to the expense of flour manufacture, and may result in damage to the baking quality if an overdosage of bleaching agent is used. The general appearance of the loaf is intimately connected with loaf volume and generally a loaf which is satisfactory in other respects will be satisfactory in appearance. High absorption is a characteristic greatly desired by bakers. However, our data show that the amount of water that a flour will absorb depends more on the environmental conditions under which the wheat is grown than on the variety. There are a few varieties, however, which vary from the normal and account of this is taken in the classification.

The final arrangement of the varieties in the order of relative baking quality was made by combining the single character classifications. Varieties with very good texture were raised above the class in which their loaf volume would have placed them. Varieties were not raised for excellence in color and appearance but were lowered if these characters were markedly faulty. Absorption had to be considered in only a few cases. Varieties which fell into Class 4 (decidedly inferior to Marquis) for any single baking characteristic were never placed higher than Class 3 (slightly inferior to Marquis) in the final classification. This was done because it was considered that a variety should not be placed in the same group with Marquis if it had any marked faults, since one such fault may be sufficient to condemn a variety commercially.

The results of this classification are given in Table XXI.

TABLE XX

CLASSIFICATION OF VARIETIES ON BASIS OF ABSORPTION

1. *Superior to Marquis*	Kota, Ceres, Ruby
2. *Equal to Marquis*	Axminster, Dicklow, Early Prolific, Early Red Fife, Early Triumph, Garnet, Hard Federation, Huron, Kitchener, Marquillo, Marquis, Parker's Selection, Pioneer, Preston, Quality, Red Bobs 222, Red Fife, Renfrew, Reward
3. *Slightly inferior to Marquis*	Supreme, Brownhead
5. *Very much inferior to Marquis*	Vermilion

TABLE XXI

CLASSIFICATION OF VARIETIES ON THE BASIS OF GENERAL BAKING QUALITY

1. *Superior to Marquis*	Reward, Ceres
2. *Equal to Marquis*	Marquis, Pioneer, Supreme, Renfrew
3. *Slightly inferior to Marquis*	Red Fife, Red Bobs 222, Early Red Fife, Ruby, Axminster, Quality, Kota, Early Triumph
4. *Decidedly inferior to Marquis*	Kitchener, Preston, Marquillo, Parker's Selection, Garnet, Huron, Brownhead, Hard Federation
5. *Very much inferior to Marquis*	Dicklow, Vermilion, Early Prolific

Milling Quality

In the study of milling quality the yield of straight grade flour and the milling properties were considered. The average flour yields obtained by the three laboratories for each sample were submitted to a variance analysis. In order to eliminate known causes of variability, the variance between years was calculated, thus making it possible to secure the three interactions, variety and place, variety and year, place and year. This made it possible to remove the significant interactions from error.

The significance of the various portions of the variance is given in Table XXII. It will be seen that the differences between the varieties in Group 3 are not significant. The interaction of variety with place is significant in only three groups and the interaction of variety and year is not significant in any of the groups. This means that the relative order of the varieties with respect to flour yield is little affected by the environment. The average results for each group are given in summary form in Table XXIII and reclassified on the basis of the significant difference in Table XXIV. Since the differences between the varieties in Group 3 are not significant, no value for the minimum significant difference can be given.

TABLE XXII

Significance of components of variance
Yield of straight flour

Group	Number of series	Ratio of Z obtained to Z at 5% point					
		Varieties (V)	Places (P)	Years (Y)	Interactions		
					V × P	V × Y	P × Y
1	16	1.3	2.4	1.5	0.0	0.0	1.9
2	16	1.1	2.3	0.0	0.6	0.0	2.6
3	14	0.7	2.2	0.0	0.0	0.0	2.7
4	12	1.7	2.0	0.6	0.0	0.0	2.8
5	8	1.9	2.2	0.6	1.2	0.6	0.9
6	8	3.8	2.9	1.8	0.1	0.0	1.9
7	6	1.8	0.0	1.4	1.0	0.0	2.1
8	12	3.4	2.5	0.0	1.2	0.2	2.2
9	12	2.9	2.0	0.0	0.1	0.2	1.6
10	14	1.2	2.6	0.9	0.0	0.0	1.8
11	6	3.3	2.9	—	—	—	—
12	5	2.9	2.7	—	—	—	—

The information in Tables XXIII and XXIV was condensed to give the classification on the basis of flour yield shown in Table XXV.

It was pointed out previously that flour yield is not the only factor in milling quality. Another classification is given in Table XXVI, which takes these other factors into account. Only a few of the varieties are abnormal in their milling or tempering behavior. Kota resembles the durums in its milling characteristics. The middlings are difficult to reduce and consequently the power required is greater than for normal varieties. Garnet requires longer tempering than the normal varieties and the middlings are more difficult to

TABLE XXIII

YIELD OF STRAIGHT FLOUR FOR EACH VARIETY IN EACH GROUP

Yield of straight flour, %	Group											
	1	2	3	4	5	6	7	8	9	10	11	12
	Minimum significant difference (%)											
	0.88	1.07	—	1.62	1.09	1.16	1.15	0.86	1.10	0.82	2.74	3.10
69.9 to 69.5						Marquillo	E. Triumph	Marquillo	Parker's Sel.			
69.4 to 69.0							Red Bobs 222				Quality	Quality
68.9 to 68.5						Red Fife E. Triumph						
68.4 to 68.0					Quality	Preston Red Bobs 222	Red Fife Supreme					
67.9 to 67.5	Red Fife	Red Bobs 222	E. Triumph			Kota Supreme	Garnet Reward Huron Ruby	Kota		Red Fife Supreme		
67.4 to 67.0	Supreme		Kota Preston	E. Triumph Kota Axminster Preston Huron	Reward Ceres	Huron Kitchener	Kitchener- Marquis		Axminster		Kota	
66.9 to 66.5	Reward Kitchener Marquis	Marquis Supreme Reward	Huron		Marquis	Marquis Garnet Reward	Renfrew	Reward	Kota	Reward Kitchener Marquis	Preston Axminster E. Triumph Ceres	Axminster Kota
66.4 to 66.0	Renfrew		Marquis Supreme Reward	Marquis	Garnet Renfrew	Renfrew		Garnet Marquis	Reward Marquis	Early R. Fife Renfrew	Huron Reward	Preston E. Triumph Ceres Pioneer
65.9 to 65.5				Reward Supreme				Renfrew			Marquis Supreme	Reward Marquis Huron
65.4 to 65.0									Renfrew		Early Prolific	Supreme
64.9 to 64.5				Hard Fed'tion							Brownhead	Early Prolific
64.4 to 64.0											Hard Fed'tion	Hard Fed'tion Brownhead
63.9 to 63.5						Dicklow						
61.4 to 61.0											Vermilion	
60.9 to 60.5												Vermilion

TABLE XXIV

Classification on basis of minimum significant difference
Yield of straight flour

Class	Group 1	2	3	4	5	6	7	8	9	10	11	12
	Minimum significant difference											
	0.88	1.07	—	1.62	1.09	1.16	1.15	0.86	1.10	0.82	2.74	3.10
+3								Marquillo	Parker's Sel.			
+2	Red Fife					Marquillo						
+1					Quality	Red Fife E. Triumph Preston Red Bobs 222	E. Triumph Red Bobs 222	Kota	Axminster	Red Fife Supreme	Quality	Quality
0	Supreme Reward Kitchener Marquis Renfrew	Red Bobs 222 Marquis Supreme Reward	E. Triumph Kota Preston Huron Marquis Supreme Reward	E. Triumph Axminster Kota Huron Marquis Reward Supreme	Reward Ceres Marquis Garnet Renfrew	Kota Supreme Huron Kitchener Marquis Garnet Reward Renfrew	Red Fife Supreme Garnet Reward Huron Ruby Kitchener Marquis Renfrew	Reward Garnet Marquis Renfrew	Reward Marquis Renfrew	Reward Kitchener Marquis Early R. Fife Renfrew	Kota Preston Axminster E. Triumph Ceres Huron Reward Marquis Supreme Early Prolific Brownhead Hard Fed'tion	Axminster Kota Preston E. Triumph Ceres Pioneer Reward Marquis Huron Supreme Early Prolific Hard Fed'tion Brownhead
−1				Hard Fed'tion							Vermilion	Vermilion
−2						Dicklow						

TABLE XXV

CLASSIFICATION OF VARIETIES ON BASIS OF YIELD OF STRAIGHT FLOUR

1. *Superior to Marquis*	Marquillo, Parker's Selection Early Triumph, Red Bobs 222, Red Fife, Quality
2. *Equal to Marquis*	Kota, Preston, Huron, Ruby, Supreme, Axminster Reward, Marquis, Kitchener, Garnet, Ceres Renfrew, Pioneer, Early Red Fife
3. *Slightly inferior to Marquis*	Brownhead, Early Prolific, Hard Federation
5. *Very much inferior to Marquis*	Vermilion, Dicklow

TABLE XXVI

CLASSIFICATION OF VARIETIES ON BASIS OF MILLING QUALITY

1. *Superior to Marquis*	Marquillo, Parker's Selection Early Triumph, Red Bobs 222, Red Fife Quality
2. *Equal to Marquis*	Preston, Huron, Ruby, Supreme, Axminster Reward, Marquis, Kitchener, Ceres Renfrew, Pioneer, Early Red Fife
3. *Slightly inferior to Marquis*	Kota, Garnet Brownhead, Early Prolific, Hard Federation
5. *Very much inferior to Marquis*	Vermilion, Dicklow

reduce, though not so difficult as those of Kota. Vermilion, Hard Federation and Dicklow have a tendency to flake rather than to grind. However, this is reflected in the low yield of straight flour and these varieties need not be further discounted on this account. The classification is given in Table XXVI.

Milling and Baking Quality

In order to arrive at a classification for milling and baking quality the classifications for milling quality and baking quality were combined. In doing this the baking quality was taken as the basis and the placing of the varieties was modified in accordance with the milling quality. Varieties with baking quality only slightly inferior to Marquis were raised if the milling quality was high. Varieties with decidedly inferior baking quality were not raised on account of high milling quality because serious defects in baking are sufficient to discredit a variety commercially. Low milling quality lowered the placing. This method of classification places the emphasis on baking quality and was adopted because in the export market high baking quality is the prime requisite in our wheats. At the same time it takes the milling quality very definitely into account. The classification is given in Table XXVII.

The first class includes varieties of excellent or good quality. If Canada's wheat crop could be restricted to these eight varieties there would be a substantial improvement in its general quality. It is fortunate that this class includes varieties with a wide range of agronomic characteristics so that there is little reason for a farmer going outside of this group in selecting a variety.

The second class includes varieties of fair quality. Unless these varieties made up a very large percentage of our crop no great harm would be done to its general quality.

TABLE XXVII

CLASSIFICATION OF VARIETIES ON THE BASIS OF SUITABILITY FOR EXPORT AND DOMESTIC MILLING

1.	Varieties which are similar to Marquis in milling characteristics and superior to, equal to or only slightly inferior to, Marquis in milling and baking quality. These varieties may be considered satisfactory for export and domestic milling. Reward, Ceres, Marquis, Pioneer, Red Fife, Renfrew, Red Bobs 222, Supreme
2.	Varieties which are similar to Marquis in milling characteristics, but which are inferior to Marquis in baking quality. These varieties may be present in a fair percentage in a mill mix without seriously affecting the quality. Early Red Fife, Ruby, Early Triumph
3.	Varieties which differ markedly from Marquis in color and shape of kernel, in milling characteristics, or are so decidedly inferior in baking quality as to depreciate seriously the commercial value of export shipments. (a) White wheats Axminster, Quality, Hard Federation (b) Varieties differing from Marquis in milling characteristics. Garnet, Kota (c) Varieties inferior to Marquis in baking characteristics. Garnet, Parker's Selection, Brownhead, Huron, Kitchener, Preston, Marquillo
4.	Varieties so decidedly inferior to Marquis in milling and baking quality as to depreciate seriously the quality of export cargoes when present in any appreciable percentage. Early Prolific, Dicklow, Vermilion

The third class includes varieties of poor quality that have been discounted for various causes. They are all objectionable in several respects. Their presence in any appreciable quantity in a cargo of wheat is bound to reduce the average quality. In view of this fact, these varieties should not be grown in western Canada. Measures should be taken to discourage the use of those that are extensively grown, whatever their agronomic characteristics may be.

It will be observed that the white wheats have been classified as unsatisfactory without regard to their placings in Tables XXI and XXVI. The presence of these varieties in our export wheat is objectionable whatever their milling and baking quality, because they cannot easily be distinguished from starchy red wheat. The quantity of white wheat grown is, and probably always will be, small. The difficulty of merchandizing small lots of wheat makes it undesirable that white wheat should be grown in western Canada, except to fill the very limited demand of biscuit flour millers. Even this is somewhat objectionable because of the almost inevitable mixing with red wheats on the farm.

The fourth class includes varieties which are decidedly bad in quality. The growing of these varieties should be actively discouraged.

Protein Content and Weight per Bushel

The protein content and weight per bushel of the varieties under study were investigated. The results were not used in the classification of the varieties for milling and baking. These characters partly determine the milling and baking quality and their effect in this regard is covered by the results of the milling and baking tests. However, because of their wide use as

indices of milling and baking quality, classifications based on them are included. These classifications were arrived at by the examination of the results of the analysis of variance of several groups of varieties. The procedure was similar to that employed in the study of the milling and baking data. As these characters are of secondary importance, only the final classifications are given.

TABLE XXVIII

CLASSIFICATION OF VARIETIES ON BASIS OF PROTEIN CONTENT

1. *Superior to Marquis*
Reward
Kota
Ceres, Ruby, Early Prolific
2. *Equal to Marquis*
Red Fife
Marquis, Marquillo, Parker's Selection, Vermilion
Pioneer, Brownhead, Preston, Axminster, Quality
3. *Slightly inferior to Marquis*
Garnet
Huron
Early Triumph
Red Bobs 222, Renfrew, Early Red Fife
Supreme, Hard Federation
Kitchener
5. *Very much inferior to Marquis*
Dicklow

TABLE XXIX

CLASSIFICATION OF VARIETIES ON BASIS OF WEIGHT PER MEASURED BUSHEL

1. *Superior to Marquis*
Reward
Kota
2. *Equal to Marquis*
Hard Federation, Axminster, Ruby, Supreme, Parker's Selection, Ceres, Quality
Marquis, Preston, Pioneer, Brownhead, Early Prolific
Huron, Red Bobs 222, Kitchener, Early Red Fife, Early Triumph, Garnet
3. *Slightly inferior to Marquis*
Red Fife, Renfrew, Marquillo
5. *Very much inferior to Marquis*
Dicklow, Vermilion

Description of Varieties

In the foregoing sections of this paper discussion of the characteristics of individual varieties has been omitted. In this section the milling and baking characteristics of each variety will be discussed and the reasons for placing certain of the varieties in a particular class in the classification pointed out. The varieties are arranged in classes and in alphabetical order within each class. It should be pointed out that the classification is based wholly on milling and baking quality, and that the practical utility of certain varieties will be limited by their agronomic characteristics.

1. *Varieties which are satisfactory for export and domestic milling*

Ceres.—This variety has satisfactory weight per bushel and a high protein content. The flour yield is equal to Marquis. It has excellent baking properties, giving a loaf of large volume and satisfactory characteristics by all formulas. The absorption is high.

Marquis.—Marquis is our standard variety and is satisfactory in all respects.

Pioneer.—This variety is similar to Marquis in weight per bushel and protein content. It gives a satisfactory yield of flour. It slightly excels Marquis in loaf volume when baked using the simple or bromate formulas. However it is not quite equal to Marquis in color of crumb.

Red Bobs 222.—Red Bobs 222 has a satisfactory test weight but only fair protein content. It gives an excellent yield of flour. The loaf volume is equal to Marquis except when the bromate formula is used and then the volume is only slightly lower. The loaves are slightly poorer in color than those of Marquis. The texture is poorer than that of Marquis when the malt-phosphate formula is used. On the whole this variety is not equal to Marquis in baking quality but its excellent flour yield entitles it to a place in this class.

Red Fife.—This variety is rather peculiar in that it has a low weight per bushel but an excellent flour yield. The protein content is satisfactory. The loaf volume is not significantly different from that of Marquis on the average. The simple formula gives a slightly lower volume. It is not equal to Marquis in texture and general appearance. Its baking quality is not as good as that of Marquis. In spite of this it is placed in this class because of its excellent flour yield. It should be pointed out that the reputation of this variety for good baking quality can probably be accounted for in part by the fact that it is late in maturing and hence its use is confined to the high quality areas.

Renfrew.—Renfrew has only moderate weight per bushel but a satisfactory flour yield. It is rather low in protein content but it is satisfactory in its baking qualities. It is equal to Marquis in loaf volume when baked with the simple or malt-phosphate formulas but it is deficient in this respect when baked with formulas containing potassium bromate. However, the texture by all methods is superior to that of Marquis and the color, appearance and absorption are satisfactory. On the whole this variety has slightly lower quality than Marquis but the difference is not sufficient to warrant placing it in a different class.

Reward.—Reward has a high weight per bushel and a satisfactory flour yield. It has a very high protein content. The baking qualities are excellent. It gives loaves of large volume with good color, texture, appearance and absorption. Reward has the best milling and baking quality of the varieties tested.

Supreme.—This variety has satisfactory test weight and milling quality. The protein content is lower than that of Marquis. It is only moderately satisfactory in baking quality. The loaf volume is lower than that of Marquis when the bromate formula is used. The texture, however, is excellent and the color and appearance are satisfactory. Supreme is slightly deficient in absorption. This variety has the poorest quality in this class.

2. *Varieties which are slightly inferior to Marquis but which may be present in a fair percentage in a mill mix without seriously affecting the quality*

Early Red Fife.—This variety has satisfactory weight per bushel and yield of flour. Its protein content is low. The absorption is satisfactory but in all the other baking characteristics it is only fair.

Early Triumph.—Early Triumph has a satisfactory weight per bushel and an excellent flour yield. Its protein content is low. The absorption is satisfactory but it is deficient in the other baking characteristics. The loaf volume and the color are not equal to Marquis and the texture and general appearance are poor. The baking quality is too low to warrant placing this variety in the first class even though the milling quality is excellent.

Ruby.—Ruby has a satisfactory test weight and flour yield. It has a high protein content and high absorption. It is only fair in loaf volume, texture and color. This variety has no outstanding defects but its quality is not sufficiently high to warrant placing it in the first class.

3. *Varieties which are unsatisfactory for export or domestic milling*

a. White Wheats

Axminster.—This variety has good test weight and milling yield. It is fair in protein content. The baking characteristics are good with the exception of color, the loaves being rather yellow.

Hard Federation.—Hard Federation has good weight per bushel but gives a low yield of flour. It is fair in protein content. It gives small loaves of rather poor appearance. The other baking characteristics are satisfactory.

Quality.—The milling quality is good. The weight per bushel and protein content are similar to those of Axminster. The loaf volume, texture and appearance are fair and the color of the crumb is good.

b. Red Wheats

Brownhead.—Brownhead is satisfactory in weight per bushel but it gives a low yield of flour. It is low in protein. The absorption is fairly satisfactory and the texture and appearance of the loaves are fair but the other baking characteristics are poor.

Garnet.—The test weight and the yield of flour are satisfactory. Garnet differs from Marquis in its tempering properties and cannot be tempered properly when mixed with that variety. For this reason the milling quality of Garnet is classed as fair. The protein content is low. It is satisfactory in absorption and in appearance of the loaves. The other baking characteristics are poor. It gives small loaves with poor texture, particularly when baked by the blend-bromate or malt-phosphate formulas. The color of the crumb is decidedly yellow. Garnet cannot be considered a desirable variety.

Huron.—The weight per bushel and the milling yield are satisfactory, but Huron is poor in all the baking characteristics with the exception of absorption.

Kitchener.—Kitchener has normal test weight and flour yield. The protein content is low. Absorption and texture are satisfactory. The appearance is fair and the loaf volume and color are decidedly poor.

Kota.—Kota has a high test weight and a satisfactory flour yield. However, since the endosperm is durum-like in character it does not mill as easily as the ordinary spring wheats. For this reason, its milling quality can only be classed as fair. It is excellent in protein content, absorption and loaf volume and the texture and appearance are satisfactory. However, the crumb has a pronounced yellow color which is objectionable. This variety has several excellent characteristics and two serious defects. It is placed in this class on account of the difficulty of milling and the color of the bread.

Marquillo.—Marquillo resembles Red Fife in that it has a low weight per bushel but an excellent milling yield. The protein content, absorption and loaf volume are satisfactory but the other baking characteristics, particularly the crumb color, are poor. In spite of the high flour yield the general quality is unsatisfactory.

Parker's Selection.—This variety, sometimes known as Parker's Marquis, is satisfactory in test weight and gives a high yield of flour. It has a normal protein content and gives a loaf which is satisfactory in absorption, volume and appearance. The texture and the color are too poor, however, to permit a higher placing. In addition, it was noticed that the handling qualities of the dough of this variety were particularly poor.

Preston.—The weight per bushel and flour yield are satisfactory. The protein content is low. The loaves have good appearance and fair volume and texture but the crumb color is poor.

4. *Varieties which are very unsatisfactory for export or domestic milling*

Dicklow.—Dicklow is low in weight per bushel and flour yield. It is very low in protein content and very poor in all the baking characteristics.

Early Prolific.—This variety has fair weight per bushel and fair milling yield. The loaf volume is poor and all the other baking characteristics are very poor.

Vermilion.—Vermilion has a fair protein content but in all other respects it can only be classed as "bad".

Acknowledgments

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STUDIES ON THE FAILURE OF HYBRID GERM CELLS TO FUNCTION IN WHEAT SPECIES CROSSES[1]

By W. P. Thompson[2] and J. M. Armstrong[3]

Abstract

Chromosome numbers were determined in numerous male gametophytes of F_1 between 21- and 14-chromosome species of wheat. The results show that pollen grains with various chromosome numbers from 14 to 21 are actually formed and in approximately the theoretically expected proportions. The lack of plants in later generations which should result from the functioning of pollen grains with intermediate numbers is therefore not due to the failure of such grains to be formed because of a lack of random segregation at the second reduction division.

Grains with intermediate numbers are retarded in their nuclear development, so that counts made on stamens in which division is most active give a smaller proportion of grains with intermediate numbers and a higher proportion with parental numbers than is expected theoretically. Retardation in nuclear development is correlated with a deficiency in cytoplasmic contents, 10 to 15% of the grains showing little or no cytoplasm, and another 15 or 20% showing some degree of reduction in cytoplasm. All grains with reduced cytoplasm and some of those with normal contents are so retarded in nuclear development (having only one or two nuclei or no organized male cells) that they could not function when the normal ones are mature and the stamen dehisces. Unfavorable chromosome conditions in grains with intermediate numbers cause a complete abortion of some grains and retardation of nuclear development in others.

Under the best available experimental conditions only 11 or 12% of F_1 pollen grains germinate, in contrast to 70 or 80% for parental pollen. No grains with reduced cytoplasm germinate, and at least 50% of those with apparently normal cytoplasm fail to germinate.

Introduction

It has been shown by Thompson and Cameron (2) and by Sax (1) that in F_1 between 21- and 14-chromosome species of wheat nearly all the male gametes which produce viable offspring have the parental chromosome numbers, or only one more or less. But to judge by events at the meiotic divisions, the great majority of the pollen grains should have intermediate chromosome numbers. Therefore nearly all those with intermediate numbers must fail to produce offspring. The great difference between the proportions of expected and functioning grains with the different chromosome numbers is illustrated graphically in Fig. 1. The female gametes with intermediate numbers are much more successful than the male.

There are several possible causes for the failure of gametes with intermediate numbers to produce viable offspring. The present paper gives the results of an attempt to determine whether certain possible causes actually have any effect, and if so, how important the effect is. The first possibility investigated is that gametes with intermediate numbers may not actually be formed in expected proportions owing to a lack of random segregation at the second reduction division. If there should be a tendency for all the 7 univalent *vulgare* chromosomes to go to one pole, the resulting pollen grains would tend to have 14 + 7 or 14 + 0 chromosomes. This would account for the results

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to be explained. The movement of the univalents seems to be a random one as observed microscopically. But hitherto no attempt has been made to determine the numbers in the pollen grains and thereby to decide whether the segregation actually is random.

The second possibility investigated is that, owing to unfavorable chromosome conditions, those with intermediate numbers may be retarded in development, or for other reasons unable to function when the others do. It is well known, of course, that 10 to 15% of the pollen is visibly abortive, but this proportion is not nearly high enough to account for the results. The apparently good pollen was therefore investigated.

Frequencies of Different Chromosome Numbers in F_1 Pollen

Methods and Materials

The chromosome numbers in the individual pollen grains were determined directly by the study of the divisions in the male gametophyte. In wheat both gametophytic divisions take place before the pollen is shed. The first produces the tube and generative cell and the second the two sperm cells from the generative cell. Mature pollen contains two well-organized, elongated male gametes.

All the counts recorded were made at the first division because the second is very difficult to study. By the time it occurs a large amount of starch has accumulated and confined the chromosomes to a compact mass. It would have been desirable to determine whether pollen of certain chromosome types fails to accomplish the second division, but, though efforts were made to do so, reliable counts were too difficult to make in sufficient numbers.

The chief difficulty in studying the first division was with the fixation, owing to the thick, hard wall of the grain and to the presence of a large vacuole. With care, satisfactory fixation was accomplished both in Nawaschin's solution and in Allen's modification of Bouin's fluid. It was necessary to remove the stamens from the flowers, to fix them alone without other floral parts, and to subject them to the suction of an air pump during a preliminary period of one or two minutes in a mixture of three parts of absolute alcohol and one of glacial acetic acid.

The plants used were hybrids between the *vulgare* variety Marquis and *dicoccum* (Vernal), *durum* (Medeah), and *persicum* (Black Persian).

Results

The counts on 189 grains from anthers in which division was proceeding actively are given in Table I, together with those to be expected on the basis of random segregation of the univalents at the second reduction division, and with those for functioning grains obtained by Thompson and Cameron by the study of plants of the next generation. In regard to 133 of the 189 grains we are quite sure of the counts; the other 56 are correct within the limits ± 1, and we believe they are fully correct. It is considered desirable to record every grain which is countable in the preparations used, in order to avoid the possibility that the ones which are most difficult to count and which might belong to

certain chromosome types are being omitted. In addition to the 189 there is a group of 37 on the same slides, in which the exact number could not be determined but which could be placed in three classes; (a) with 14 or 15, (b) with 16 to 19, (c) with 20 or 21. The frequency distribution of these is not different from that of corresponding groups recorded in Table I.

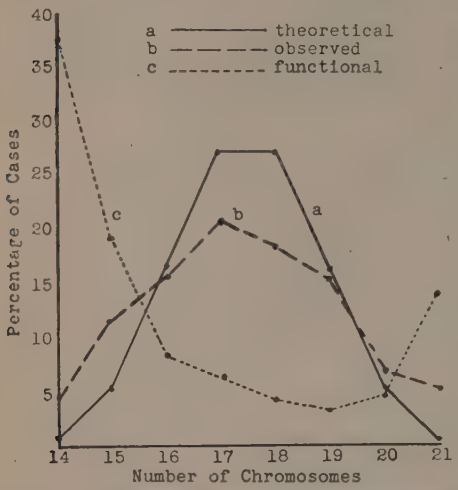

FIG. 1. *Frequency distribution of chromosome numbers in F_1 pollen grains; a, theoretical; b, observed; c, functional.*

It is plain that the actual frequency of the different chromosome numbers is, in a general way, similar to that which would be expected if the seven univalent *vulgare* chromosomes move at random to either pole at the second reduction division. It is very different, however, from that of the pollen grains which function successfully (or at least produce viable offspring) as determined by Thompson and Cameron and by Sax. These points are illustrated graphically in Fig. 1. The curve for the actual counts (b) is of the same general form as that expected (a), but the curve for the functional grains is inverted (c). These curves show that all chromosome types of pollen grains are actually produced approximately in the proportions expected on the basis of random segregation, but that the great majority of those with intermediate numbers do not function, or at any rate, do not produce viable offspring.

TABLE I

FREQUENCIES OF CHROMOSOME NUMBERS IN POLLEN GRAINS OF F_1

Cross	Chromosome number								Totals
	14	15	16	17	18	19	20	21	
vulgare × dicoccum	3	6	14	15	9	12	4	3	61
vulgare × durum	1	7	7	9	8	4	2	1	39
vulgare × persicum	4	9	8	15	19	15	7	7	84
Totals	8	22	29	39	36	31	13	11	
Percentages	4.2	11.7	15.3	20.7	19.0	16.4	6.9	5.8	189
Expected	0.8	5.5	16.4	27.3	27.3	16.4	5.5	0.8	
Functional	37.7	19.3	8.8	7.0	4.4	3.5	5.2	14.0	

Although there is a general similarity between the actual and expected results, nevertheless there is a noticeable deficiency of grains with intermediate numbers and an excess of those with extreme numbers (14 and 15, 20 and 21)

recorded in Table I. Curve (b) of Fig. 1 begins and ends at a higher level than curve (a), but does not rise as high. The expected ratio of grains with the extreme numbers 14, 15, 20 and 21, to those with the intermediate numbers 16, 17, 18 and 19, is 1 to 7.5. The actual ratio is 1 to 2.5.

It was considered possible that grains with intermediate numbers might appear to be deficient because they might develop slowly owing to their unfavorable chromosome combinations. The spread in the time of division among different grains of the same pollen sac is much greater than among pollen mother cells. The counts recorded in Table I were made on stamens in which a considerable proportion of the grains were actively dividing. The grains which were late in dividing owing to unfavorable chromosome conditions would be missed from such counts. In order to test this possibility stamens were studied in which nearly all the grains had divided (were already binucleate). Chromosome counts were made on the few that were still dividing. The frequencies of the chromosome numbers in these retarded grains are shown in Table II.

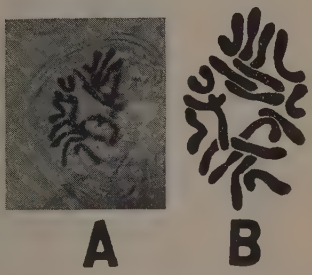

FIG. 2. *A. Photomicrograph of first gametophytic division in a pollen grain with 19 chromosomes. ×900. B. The same; camera lucida drawing.*

TABLE II

FREQUENCIES OF CHROMOSOME NUMBERS IN F_1 GRAINS WHICH WERE RETARDED IN DEVELOPMENT

Chromosome numbers	14	15	16	17	18	19	20	21	Total
Frequency		1	5	12	14	6	2		40

It is plain from this table that the grains which develop slowly usually have intermediate numbers. Apparently the chromosome conditions in such grains are unfavorable for vigorous development. The deficiency of intermediate numbers in counts made when division figures are abundant would therefore be explained. It will be shown later that many of the tardy grains never reach the stage of the first division but remain uninucleate and that others which pass the first division fail to reach the second or to form sperms.

Another general feature of the results is that there are more grains in the four lowest number classes (with 14 to 17 chromosomes) than in the four highest (18 to 21). This is particularly striking in *vulgare* × *dicoccum* and *vulgare* × *durum*. The cause is doubtless the loss of lagging univalent chromosomes which fail to reach the poles at the homotypic division in time to be included in the daughter nuclei. This would cause a general reduction in chromosome numbers (Watkins (4), Thompson and Hollingshead (3)).

Relation Between Cytoplasmic Content and Nuclear Development of Pollen Grains

It was shown in the previous section that there is great variation in the rate of early development of the pollen grains and that the slower grains have intermediate numbers. It is therefore desirable to trace the later development and ultimate fate of such grains.

Methods

Stamens at various stages between the completion of the meiotic divisions and maturity were fixed as previously described and preserved in 70% alcohol. The examination was made in smear preparations in aceto-carmine. This made possible the study both of cytoplasmic and nuclear conditions in well-fixed grains at all stages of development. Caution is necessary in the study of mature grains by this method because in some of them the wall bursts and is likely to be thrown off and appear as an empty grain.

Development of Pollen Grains

(a) *Normal*

Following the meiotic divisions the young pollen grains contain a rather dense cytoplasm with no vacuoles. Then follows a period of rapid enlargement which is not accompanied by a corresponding increase in the amount of cytoplasm. The result is the appearance of a large vacuole which occupies most of the space in the young grain, the cytoplasm being confined to a thin layer at the periphery (Fig. 3, A). In normally developing grains the vacuole then gradually becomes filled with cytoplasm. As soon as this process is completed, starch is deposited and eventually is present in a dense mass.

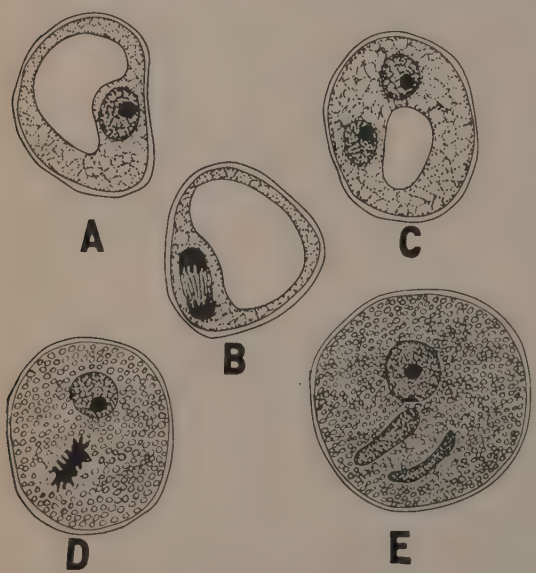

Fig. 3. *Different stages in the normal development of a pollen grain of wheat (see text).*

The first gametophytic division, which forms the tube and generative cells, takes place while the vacuole is still of considerable size (Fig. 3, B). The second division occurs after the vacuole has been filled and a large amount of starch has been deposited (Fig. 3, D). The two sperm nuclei which result from this division only gradually assume the characteristic elongated form (Fig. 3, E).

In most species and hybrids the first division takes place in the oldest flower of the oldest spikelets at the time the spike is pushing through the sheath. Periods of about two days elapse between the first and second divisions and between the second division and the maturity of the pollen. The spikelets at the tip and base of the spike lag a day or so behind those at the centre in respect to all these events.

(b) *Abnormal*

In the F_1 all pollen grains appear to develop normally until the large vacuole is present. In many of them the development then becomes abnormal in that the cytoplasm does not increase sufficiently to fill the vacuole. In some the cytoplasm not only fails to increase but degenerates at an early stage, so that it has disappeared by the time that those which develop normally have reached the stage of the first division. In others the cytoplasm increases very slowly; these lag further and further behind the normal ones. In different grains there are various rates of cytoplasmic increase and many apparently cease developing entirely at various stages. Consequently in mature stamens various amounts of cytoplasm may be observed in different grains, from the normal dense mass to none at all.

The grains in anthers at certain stages of development were classified according to their cytoplasmic content into four groups; those with normal, reduced, slight, and no cytoplasm. The percentages of grains in these four classes at the stage when the first gametophytic division is most abundant are given in Table III. Even in pure species there is a small percentage of grains with less than the normal amount of cytoplasm, but in the hybrids the percentage is much higher. It is notable that the sum of the percentages in the classes "slight" and "none" is nearly equal to the percentage of visibly aborted mature pollen as reported by several authors. Evidently most of the grains that will completely abort can be recognized at this stage.

TABLE III

PERCENTAGES OF GRAINS WITH VARIOUS AMOUNTS OF CYTOPLASM IN ANTHERS IN WHICH THE FIRST GAMETOPHYTIC DIVISION IS TAKING PLACE

Material	Cytoplasmic condition				Total
	Normal	Reduced	Slight	None	
vulgare	92.8	4.8	1.6	0.8	842
dicoccum	82.6	13.4	3.2	0.8	522
persicum	88.9	9.1	1.7	0.3	736
F_1 vulgare × dicoccum	56.1	33.0	9.3	1.6	1653
F_1 vulgare × durum	58.1	27.7	12.8	1.4	1343
F_1 vulgare × persicum	66.6	24.9	6.6	1.9	1350

Nuclear Conditions in Various Pollen Types

In the previous reports regarding abnormal or abortive pollen in crosses of this type, no account has been taken of nuclear conditions. When methods are used which reveal the condition of the nuclei as well as that of the cytoplasm,

a strong correlation becomes evident between the amount of cytoplasm and the degree of nuclear development, even where the reduction in the amount of cytoplasm is small. This is shown in the accompanying tables.

TABLE IV

PERCENTAGE OF F_1 POLLEN GRAINS OF VARIOUS CYTOPLASMIC TYPES THAT WERE *uninucleate* (REST BINUCLEATE) WHEN SOME WERE UNDERGOING FIRST GAMETOPHYTIC DIVISION

Material	Cytoplasmic condition			
	Normal	Reduced	Slight	None
vulgare × dicoccum				
stamen 1	11.2	35.9	90.5	100.0
stamen 2	52.2	61.2	89.0	100.0
stamen 3	22.5	47.9	88.2	100.0
vulgare × durum				
stamen 1	19.7	43.9	85.7	100.0
stamen 2	9.5	43.2	89.4	100.0
stamen 3	5.9	33 6	91.2	100 0

The data in Table IV were collected from stamens in which many of the grains were undergoing the first division. It shows the percentage of grains in each of the four cytoplasmic classes which were uninucleate at that time, the rest being binucleate. The stamens are recorded individually since the percentage of uninucleate grains decreases with the development of the stamen. It is plain that the less cytoplasm there is in a grain, the more retarded is the nuclear development. None of those which lacked cytoplasm and only a small percentage with a "slight" amount had divided, whereas the great majority of those with a normal amount had done so.

Similar results were obtained at a later stage when the second division was occurring in some of the grains. Table V gives the results for one stamen which was typical of many studied. Those in the class "three nuclei" were ones in which the generative nucleus had divided but in which the daughter nuclei had not yet been organized as sperms. The majority of those with normal cytoplasm already possessed sperms and nearly all had divided twice; but few of

TABLE V

RELATION BETWEEN NUCLEAR DEVELOPMENT AND CYTOPLASMIC CONDITION IN F_1 POLLEN WHEN SECOND GAMETOPHYTIC DIVISION IS OCCURRING (VULGARE × PERSICUM)

Nuclei	Cytoplasm			
	Normal	Reduced	Slight	None
Sperms present	56.8	1.0		
Three nuclei	31.0	7.3		
Two nuclei	11 5	87.4	26.6	
One nucleus	0.7	4.3	73.4	100 0
	100.0	100.0	100.0	100.0

those with reduced and none with slight or no cytoplasm had undergone the second division. It is not at all probable that those in the last three groups would be able to function by the time the pollen was shed, even if they developed further.

TABLE VI

RELATION OF NUCLEAR DEVELOPMENT AND CYTOPLASMIC CONDITION IN POLLEN AT SHEDDING TIME

Material	Cytoplasm	Nuclei					Per cent
		Sperms	3	2	1	Empty	
dicoccum	Normal	1850	9	4	1		95.3
	Reduced	4	8	12	5		1.5
	Slight		3	20	12		1.8
	None					29	1.5
	Per cent	94.8	1.0	1.8	0.9	1.5	
F_1 vulgare × dicoccum	Normal	925	63	45			76.1
	Reduced	59	117	6			13.5
	Slight		5	21	23		3.6
	None					92	6.8
	Per cent	72.7	13.6	5.3	1.7	6.8	
F_1 vulgare × durum	Normal	817	92	97	1		64.5
	Reduced	40	62	187	36		20.7
	Slight		26	61	72		10.2
	None					71	4.6
	Per cent	54.9	11.5	22.1	6.9	4.6	
F_1 vulgare × persicum	Normal	1652	88	63			73.3
	Reduced	62	145	113	31		14.2
	Slight		19	79	82		7.3
	None					126	5.1
	Per cent	69.6	10.2	10.4	4.6	5.1	

Finally, the conditions in pollen of mature stamens which were about to dehisce are shown in Table VI. From 27 to 45% of the F_1 pollen had not yet organized sperms and would be unable to function. As at earlier stages, most of those which were retarded in nuclear development showed some degree of reduction in cytoplasmic contents, but a considerable proportion which appeared normal with respect to the cytoplasm were still without properly organized sperms even at this late stage.

Several investigators have reported that the percentage of bad pollen in these hybrids is from 10 to 15. From the data in Table VI it appears that in those papers only that pollen was reported as bad which we have classified as having little or no cytoplasm. The previous accounts apparently did not distinguish from the normal, the 15 to 20% with a "reduced" amount of cytoplasm. Most of these "reduced" grains have no properly organized sperms and many have not even undergone the sperm division at the time the pollen is shed. It is very doubtful whether they would be ready to germinate and certain that they would not compete successfully with the normal grains which possess sperms. To the frequently reported 10 or 15% obviously

sterile pollen should therefore be added the 15 or 20% with reduced cytoplasm and retarded nuclear development. In addition about 10% of the grains with apparently normal cytoplasm (6 or 7% of all grains) are also retarded in nuclear development.

It was shown in an earlier section that the grains in which the nuclear development is retarded have chromosome numbers intermediate between those of the parents. This is one cause of the failure to function on the part of many grains with intermediate numbers. The chromosome combination may be so unfavorable as to cause the early abortion of some grains, or it may only retard their development so that they are not ready to function at the time the pollen is shed.

Germination of Pollen

In the previous section it was shown that in addition to the obviously sterile pollen grains there are many in which the nuclear development is so retarded that they would probably not be ready to germinate when the anthers dehisce. Experiments were therefore carried on to test the germination of F_1 pollen in comparison with that of the parents. Watkins (4) experimented on *vulgare* × *turgidum* pollen and extracts from his report are as follows: "With regard to the actual proportion of pollen that germinates it is difficult to reach a definite conclusion.... Allowing a proportion of 0.2 for aborted grains and assuming, in accordance with the indications of Table 8 that about 80 per cent of the pollen that was able to germinate had done so, we may put the proportion of F_1 pollen that can germinate on F_1 stigmas at about 0.10. Similarly on Rivet (*turgidum*) stigmas it appears that germination may be as high as about 30 per cent." On *vulgare* (Lion) it was only 5%.

Methods

Numerous unsuccessful attempts were made to germinate wheat pollen in various solutions at different concentrations. The results were no better with agar and sugar. Some success was attained by dusting the dry pollen on a coverglass and inverting it over a moist cell, but the results were not consistent and no way could be found of controlling conditions so as to obtain consistent results.

The authors then adopted the method of examining stigmas which had been pollinated previously. This had the advantage that conditions were more nearly natural, but also the disadvantage that some ungerminated grains might be lost in handling. Special experiments designed to test the latter point showed, however, that the loss was negligible when proper methods of handling were used.

Many preliminary experiments were carried on in order to test fixatives, stains and methods of handling, to determine when the stigmas were most receptive and how long it took the grains to germinate. The procedure finally adopted was as follows:

The spikes which were to furnish the stigmas were emasculated and protected when just clear of the sheath, 20 flowers from the 10 central spikelets being

used and the rest removed. Three to five days later when the stigmas were fully receptive, as judged by their well-feathered condition and by the separation of lemma and palea, they were artificially pollinated. To ensure that the pollen was fully mature and all types of grains properly represented, spikes were chosen in which some anthers had already dehisced. The tops were clipped from neighboring spikelets and the ripe stamens which emerged immediately were used individually. The spikes were then protected.

Ten to twelve hours later the stigmas were removed and all from one spike mounted on a slide. In order to reduce handling to a minimum they were mounted in a medium which acted both as fixative and stain, the most successful being lactic phenol colored with methylene blue. The best four to six stigmas on a slide were selected, the choice depending on a favorable number and distribution of grains and on relatively good germination (this indicating good receptivity of the stigma).

Owing to the much branched, feathery nature of the wheat stigma it was impossible to make a satisfactory study of the relative rates of pollen tube growth.

Results

In spite of the greatest care, different preparations of the same kind of material show considerable variation in the percentage of germination. The greatest variation among the stigmas of one F_1 plant pollinated by F_1 pollen is from 8.3 to 23.1%. And among all the 36 stigmas of this type on which full counts were made the variation is from 6.8 to 27.4. These variations apparently depend on varying degrees of receptivity of the stigmas and of moisture content of the flowers. In view of the number of grains examined and the consistency of the differences between F_1 and parental pollen, the authors believe the results give an approximately correct picture of the situation.

TABLE VII

Germination of pollen

Pollen	Stigmas	Per cent ungerminated grains of different cytoplasmic types						Germinated	Number of grains
		Normal	Reduced	Slight	None	Burst	Total		
vulgare 1	vulgare 1	5.9	3.4	1.7	5.9	6.3	23.3	76.7	236
vulgare 2	vulgare 2	4.7	2.9		3.2	1.5	12.3	87.7	339
dicoccum	dicoccum	14.6	1.9	1.3	3.9	8.1	29.9	70.1	308
persicum	persicum	9.8	3.3	1.3	9.8	2.6	26.8	73.2	153
vulgare 2	F_1	4.3	2.9	1.1	2.5	0.9	11.7	88.3	310
F_1	dicoccum	26.6	16.9	14.1	7.6	13.3	77.2	22.8	424
F_1 (dicoccum) (1)	F_1 (dicoccum)	37.9	28.1	10.7	4.6	7.4	88.7	11.3	327
F_1 (durum)	F_1 (durum)	31.6	21.4	17.3	13.8	4.6	88.8	11.2	916
F_1 (persicum)	F_1 (persicum)	41.2	15.5	12.0	7.3	11.2	87.4	12.6	658
F_1 (average)	In stamen	71.5	15.9	7.2	5.4				4378

(1) *All hybrids are between vulgare and the species mentioned.*

The data are summarized in Table VII. The grains recorded as germinated include those in which only the tip of the tube had protruded. The ratio of such grains to those with well-developed tubes is about 1 to 6. It is of course impossible to classify the germinated grains according to their cytoplasmic contents as is done in the case of the ungerminated grains because the cytoplasm of the former moves into the tube. The bursting of a small percentage of the grains apparently occurs in the flowers before the removal of the stigmas, although a small amount of it may be due to the handling.

The table shows that, under the conditions described, 70 to 88% of parental pollen grains germinate, but that only 11 or 12% of the pollen of three kinds of F_1 germinate on F_1 stigmas. These percentages are in agreement with the general conclusions reached by Watkins.

The ungerminated grains with less than the normal amount of cytoplasm constitute a somewhat higher percentage of all grains than is the case when the pollen is shed. This shows that none of the grains which are deficient in cytoplasm are able to germinate, even though the deficiency is slight. In addition there must be some influence which raises the proportion of cytoplasm-deficient grains above that found at pollination time. No evidence could be found that this was due to the falling-off of grains with normal cytoplasm. It may be due to swelling of grains on the stigma or to errors in classification. Some of the grains which had germinated and given up part or all of their cytoplasm to the tube may have become detached from the tube in handling, and recorded as ungerminated and deficient in cytoplasm. In some cases also the position of the germination pore may have been such as to make detection of the tube difficult. The percentage of germination in all cases may therefore have been somewhat higher than recorded. But even the maximum allowance for these causes would leave the germination of F_1 pollen less than 25%.

Besides those with deficient cytoplasm the ungerminated grains include a surprisingly high percentage of those with apparently normal cytoplasm. About 70% of mature pollen grains, still in the stamens, are normal in their cytoplasmic content; about 35% of all grains that have been in contact with stigmas are normal in cytoplasm and ungerminated. Consequently only about 50% of apparently normal grains germinate. It has been shown in a previous section, however, that about 10% of such grains with normal cytoplasm had not formed their sperms by shedding time. After allowance is made for these a high percentage, apparently normal in both cytoplasm and nuclei fail to germinate.

An examination of Table VII shows that the F_1 pollen germinates better on parental than on F_1 stigmas (22:11%). The difference is large enough to be significant. It cannot be attributed to unfavorable physical conditions in F_1 flowers, because parental pollen germinates equally well on F_1 and parental stigmas, as may be seen in the table. It appears, therefore, that the mutual relationship between F_1 pollen and F_1 stigmas is less favorable than that between the same pollen and parental stigmas.

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INHERITANCE OF RESISTANCE TO FOWL PARALYSIS (*NEUROLYMPHOMATOSIS GALLINARUM*)

II. ON A SIGNIFICANT DIFFERENCE IN THE INCIDENCE OF FOWL PARALYSIS IN TWO GROUPS OF CHICKS[1]

By Jacob Biely[2], Elvira Palmer[3] and V. S. Asmundson[4]

Abstract

Data are presented on two groups of thirty chicks each, hatched from a susceptible and an apparently resistant flock. There was a significant difference in the incidence of fowl paralysis and lymphomatous tumors in these two groups. This is interpreted to mean that there is an inherent difference in susceptibility and resistance to fowl paralysis and lymphomatous tumors.

Comparatively little nformation is as yet available regarding the mode of transmission of fowl paralysis (*Neurolymphomatosis gallinarum*). Pappenheimer, Dunn and Seidlin (8) are the only investigators who have reported success in transmitting fowl paralysis by artificial inoculation of newly hatched chicks. They report that typical lesions were found in approximately 25% of the inoculated chicks, while in control chicks kept under laboratory conditions the incidence of the disease was about 7%. These investigators have also observed that some of the experimentally inoculated chicks developed lymphomatous tumors. It may be noted that Mathews and Walkey (5) are of the opinion that there is no connection between paralysis and the common lymphadenomas of the fowl. They further state that these are inherited as a simple Mendelian recessive.

Doyle (3) reported that several birds hatched from eggs laid by an affected flock developed typical paralysis and iritis. The first case of paralysis occurred at 47 days of age. Control birds kept under observation until ten months of age did not show evidence of neuritis or paralysis. Doyle states, "It appears more than probable, then, that paralysis may be transmitted from parent to offspring in much the same way as bacillary white diarrhoea."

Marginson and McGaughey (4) report that the histories of 17 outbreaks of fowl paralysis afford strong evidence that the disease may be transmitted through the egg and by young chicks. Beaudette and Hudson (2) state that "while there is much to be done before the question of transmission can be finally settled, the evidence at hand (based on field observations) is strongly in favor of the conception of transmission through the egg". These authors are also of the opinion that the appearance of paralysis on a hitherto non-infected farm is always preceded by the introduction of hatching eggs, baby chicks, or breeding stock from an affected flock.

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The present report deals with one phase of the authors' investigations conducted during the past year, namely, the incidence of fowl paralysis and lymphomatous tumors in chicks hatched from (1) a paralysis affected flock, and (2) a flock apparently free from paralysis.

Material

The breeding flock used in this investigation consisted of 119 Rhode Island Red pullets mated to 6 Black Orpington males. Data presented in a previous report (Asmundson and Biely (1)) dealing with the inheritance of resistance to fowl paralysis, showed that 49 of these 119 pullets belonged to families free of paralysis and lymphomatous tumors. Seventy pullets belonged to families in which paralysis or lymphomatous tumors were known to be present. Of these seventy, 51 appeared to be normal, 13 became paralyzed, 2 had lymphomatous tumors only, and 4 showed paralysis and lymphomatous tumors.

Of the six males, two were from apparently resistant families. The other four were from two susceptible families. In the latter group out of thirteen sisters in one family, one became paralyzed, while out of seven sisters in the second family one became paralyzed and one died from lymphomatous tumors.

Eggs from the flock of 119 Rhode Island Red pullets were collected in November and December. At that time several birds died from paralysis and lymphomatous tumors. Some of the birds which laid during the period when the eggs were collected for hatching subsequently developed paralysis or died from tumors. Undoubtedly, therefore, some of the eggs laid by these pullets were incubated with the eggs used in this experiment, although pedigrees are not available to prove this.

The chicks from the above mating hatched January 1, 1931, and were transferred to wire battery brooders placed in a separate room, in a building where a few normal and paralyzed birds were kept in cohabitation.

The first case of paralysis in these chicks developed at the end of exactly eight weeks, or 56 days, while the birds were still in the battery brooder. Since the birds grew rapidly and were too large for the battery brooders, some were disposed of, while 30 well-grown chicks were placed in a separate house and kept on a wire floor.

Experimental

Group 1

On March 20, when the birds were 79 days old, one of the 30 birds developed paralysis of the left leg, and on post-mortem examination showed gross lesions in the brachial plexus, the spinal cord, the lumbo-sacral plexus, sciatic nerves, and a lymphomatous tumor of the ovary (Fig. 5). Considering the age of this bird, the gross lesions were very marked and extensive. Photomicrographs showing the massive lymphoid infiltration of the nervous system of this bird are presented in Figs. 1, 2, 3 and 4, and of the ovary in Fig. 6. These figures illustrate the typical conditions observed in affected birds.

The clinical symptoms and gross lesions of the 30 birds are shown in detail in Table I, and summarized in Table II. Thirteen females and nine males were examined before May 15. Of the 13 females 7 became paralyzed and showed gross lesions in the nervous system, and four of these also showed lymphomatous tumors of the ovary. Two of the remaining six birds showed lymphomatous tumors of the ovary, but did not show any gross lesions in the nervous system.

TABLE I

INCIDENCE OF PARALYSIS AND LYMPHOMATOUS TUMORS IN CHICKS HATCHED FROM A FLOCK AFFECTED WITH PARALYSIS

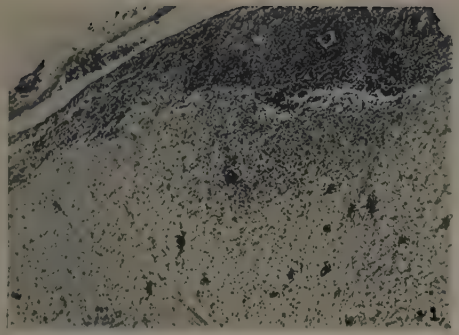
Sex[1]	Number of bird	Description	Age in days	Gross lesions in the nervous system[2]	Lymphomatous tumors[3]
F	715	Paralyzed	79	X	X
F	676	Died	81	—	X
F	723	Paralyzed	89	X	X
F	607	Died	92	—	—
F	662	Paralyzed	96	X	X
F	633	Paralyzed	97	X	—
F	689	Paralyzed	98	X	X
M	687	Killed	100	?[4]	—
M	612	Paralyzed	103	X	—
M	620	Paralyzed	107	X	—
M	660	Killed	107	—	—
M	711	Killed	110	—	—
M	688	Killed	110	?	—
M	682	Killed	110	?	—
M	622	Killed	110	?	—
F	692	Paralyzed	119	X	—
M	699	Killed	125	—	—
F	695	Killed	126	—	—
F	679	Killed	126	—	—
F	657	Paralyzed	126	X	—
F	611	Killed	132	—	—
F	685	Killed	132	—	X
F	675[5]	Died	200	—	—
F	678	Killed	215	—	—
F	680	Died	240	—	X
F	700	Killed	250	—	—
F	655	Killed	286	—	X
F	702	Killed	328	—	X
F	677	Killed	336	—	—
F	770	Killed	353	—	X

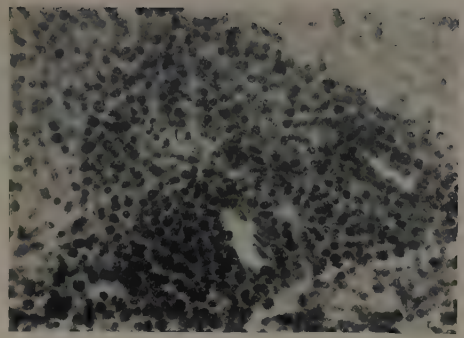
[1] *F = female; M = male.* [2] *X = lesions visible to the naked eye.* [3] *X = tumors visible to the naked eye.* [4] *? = lesions confined to the brachial plexus.* [5] *The last eight birds in this table are not strictly comparable to Group 2 in Tables III and IV since they were kept for more than 145 days.*

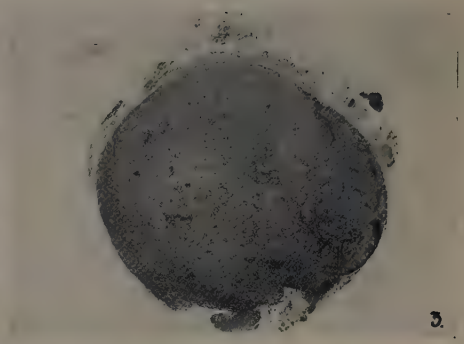
TABLE II

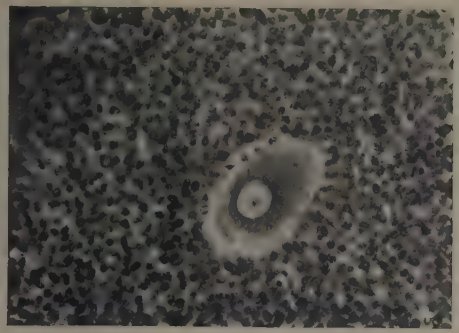
SUMMARY OF TABLE I

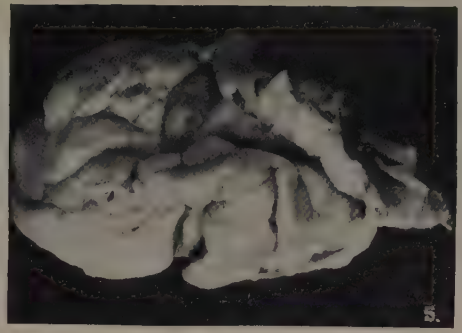
Number of birds		Paralysis only	Paralysis and tumors	Tumors only	No tumors or paralysis
Females	21	3	4	6	8
Males	9	2	0	0	7
Total	30	5	4	6	15











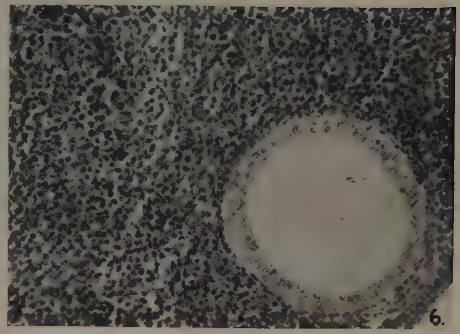


FIG. 1. *Bird No. 715. Cross section of spinal cord showing massive perivascular and interstitial lymphoid infiltration.* FIG. 2. *Bird No. 715. Dense perivascular lymphoid infiltration in spinal cord (high power).* FIG. 3. *Bird No. 715. Brachial nerve root. Note almost complete replacement of nerve tissue by lymphoid cells.* FIG. 4. *Bird No. 715. Higher magnification of a part of the section shown in Fig. 3. Note the density of the infiltration and the uniform distribution of the lymphoid cells.* FIG. 5. *Bird No. 715. Lymphomatous tumor of the ovary.* FIG. 6. *Bird No. 715. Cross section of lymphomatous tumor of the ovary.*

PLATE I

Two of the nine males were paralyzed and showed gross lesions in the nervous system. The remaining seven males were apparently normal, but on post-mortem examination four of these showed gross lesions in the brachial plexus. Had these seven birds been kept for a longer period they would possibly have developed paralysis.

The remaining eight pullets from this group of thirty began to lay when five months of age and were placed in a newly built house on clean ground. Two birds died from intercurrent causes; in one of these the ovary presented a lymphomatous condition. Two were killed because they were crop-bound. The remaining four showed definite signs of emaciation, diarrhea, and on post-mortem examination, characteristic lymphomatous tumors (about 3 to 4 inches in diameter) were found in the ovaries of three birds and generalized lymphomatous tumors in the fourth bird.

It is interesting to note that four Single Comb White Leghorn pullets, of unknown ancestry, and a male bird kept in the same pen with these eight pullets from May 25 to date (December 19), appear to be in excellent condition.

Group 2 (Control Chicks)

S.C.W. Leghorn chicks secured from a flock in which paralysis had not occurred *in previous years* served as controls. It should be noted, however, that out of approximately 2000 chicks hatched on this farm, four developed paralysis late in the spring and six adult birds developed paralysis in the autumn and winter. Furthermore, 8 to 9% of the chicks sold from this

TABLE III

INCIDENCE OF FOWL PARALYSIS IN INOCULATED CHICKS

No. of chick	Route and order of inoculation				Killed or died (age in days)	Lesions in nervous system[1]
	Leg cc.	Leg cc.	Breast cc.	Brain and leg cc.		
2488	0.5	0.5	0.5	0.2	60	—
74	0.5	0.5	0.5	0.2	84	—
157	0.5	0.5	0.5	0.2	96	—
55	0.5	0.5	0.5	0.2	102	—
91	0.5	0.5	0.5	0.2	102	—
81	0.5	0.5	0.5	0.2	104	—
96	0.5	0.5	0.5	0.2	104	—
87	0.5	0.5	0.5	0.2	124	—
84	0.5	0.5	0.5	0.2	124	—
		Brain	*Breast*	*Leg*		
2486		0.2	0.5	0.5	56	—
86		0.2	0.5	0.5	68	—
187		0.2	0.5	0.5	75[2]	X
27		0.2	0.5	0 5	103	—
2476		0.2	0.5	0 5	104	—
89		0 2	0.5	0.5	124	—

[1] — = *no lesions visible to the naked eye; X = lesions visible to the naked eye.*
[2] = *paralysis at 75 days.*
NOTE:—*The inoculations were performed when the chicks were 7-14 days old.*

flock to a farm where paralysis was prevalent for the past three years developed paralysis. No losses have been reported by others who purchased chicks from this farm.

The chicks secured as controls were raised in a wire battery brooder placed in a room opposite to the one in which the crossbred chicks (susceptible strain) were raised. One group of chicks (Lot A) was inoculated and kept in the upper deck of the battery brooder, while the other group (Lot B), which was not inoculated, was kept in a lower deck.

TABLE IV

INCIDENCE OF PARALYSIS AND LYMPHOMATOUS TUMORS IN UNINOCULATED CHICKS

Number of chicks	Killed or died (age in days)	Gross lesions in nervous system	Lymphomatous tumors[1]
1	60	—	—
1	96	—	X
1	102	—	—
2	104	—	—
3	128	—	—
3	134	—	—
4	145	—	—

[1]—=*no lesions visible to the naked eye; X=lymphomatous tumor of the ovary present.*

NOTE:—*There was no paralysis in this group of chicks.*

The chicks of Lot A were inoculated four times within a week, twice in the leg, once in the breast, and once n the brain and leg. The inoculum, which consisted of heavy suspensions of nervous tissue obtained from paralyzed birds, was freshly prepared prior to each series of inoculations. Table III shows the route of inoculation and the age at which the chicks died or were killed. It will be seen that one chick, No. 187, developed paralysis at 75 days, with gross lesions in the nervous system. The remainder did not show paralysis or gross lesions on post-mortem examination.

Table IV shows the age at which the uninoculated chicks (Lot B) died or were killed. None of the chicks developed paralysis or showed gross lesions in the nervous system. One chick, No. 2479, showed lymphomatous tumors, without paralysis, at 96 days. The remainder appeared normal on post-mortem examination.

Discussion

The data on the two groups of chicks, which were based on clinical symptoms and careful post-mortem examinations, are presented in Tables I, III and IV. Only chicks that died or were killed at certain intervals, after 56 days, were examined. The majority of the chicks were over two and one-half months (75 days) of age, when examined. The observations, except in the case of eight pullets (Table I) were concluded before the chicks were 145 days old. While this period of observation may not have been long enough to permit paralysis to develop in all cases, since the disease may occur up to 15 months of age, it undoubtedly includes the large majority of cases.

It is apparent from a study of the data in Tables I to IV that there was considerable difference in the incidence of paralysis and tumors in the two

groups of chicks. Thus 11 out of 30 chicks (Group 1), or 37%, hatched from a susceptible flock, showed paralysis, paralysis with tumors, or tumors only; whereas in Group 2, 1 of the 15 inoculated chicks developed paralysis, and 1 of the 15 uninoculated chicks developed a lymphomatous tumor. Thus only 2 out of the 30 chicks, or 6.6%, in Group 2 showed fowl paralysis or lymphomatous tumors, as contrasted with 11* out of the 30 chicks hatched from the susceptible flock. The difference in the incidence of paralysis and tumors in these two groups appears to be significant. This agrees with data presented in a previous paper (Asmundson and Biely, (1)) which indicated that resistance or susceptibility to fowl paralysis is inherited.

It is evident that neither the severe inoculation, repeated four times, with heavy suspensions of nervous tissue from paralyzed birds, nor the fact that the chicks were housed in a building in which paralyzed birds were kept, appeared to influence the resistance of the majority of the chicks to paralysis. In any large population there are likely to be susceptible individuals, and it is not improbable that the two birds (inoculated and uninoculated) that developed paralysis or lymphomatous tumors, were susceptible to fowl paralysis. The possibility of the presence of a small proportion of susceptible chicks among the controls is further indicated by the fact already mentioned that about 8% of the chicks, raised on a farm where paralysis was endemic, developed the disease.

It is of considerable importance to determine whether, as suggested by Doyle, paralysis can be transmitted from the parent stock to the progeny through the egg. Our data do not permit definite conclusions on this point. Nevertheless the early appearance of paralysis and gross lesions in the nervous system of some of the chicks points to transmission through the egg.

It is interesting to note, in connection with the chicks hatched from the susceptible stock, that the parent stock did not develop paralysis until they were from 5 to 10 months old, while the progeny developed paralysis and gross lymphomatous lesions at a comparatively early age, or less than three months. Both paralysis and lymphomatous tumors occurred at about the same age, possibly indicating that the incubation period of the two conditions is about the same (2 to 10 months). The relation of the tumors to paralysis will be discussed in a subsequent paper.

While the relation of fowl paralysis and lymphomatous tumors cannot be determined on the basis of the data presented in this and a previous paper (1) it is of interest to note that in the groups so far studied both tend to occur together more frequently than would be expected on the basis of chance. Finally, the data presented in this paper also furnish additional evidence in favor of the view that resistance and susceptibility to fowl paralysis and lymphomatous tumors are inherited.

** Four cases of lymphomatous tumor occurred in the eight birds which were kept after 145 days of observation, making a total of 15 affected birds (see Table I).*

Summary

1. The data reported in this paper were based on two groups of chicks observed for periods ranging from 60 to 145 days. Group 1 was hatched from a susceptible flock, while Group 2 was hatched from an apparently resistant flock.

2. Out of 30 chicks from Group 1, 5 developed paralysis only, 4 paralysis with lymphomatous tumors, and 2 lymphomatous tumors only, making a total of 11 affected chicks. Four apparently normal males showed gross lesions in the brachial plexus.

3. Out of 15 inoculated chicks of Group 2, 1 developed paralysis; and out of 15 uninoculated chicks of Group 2, 1 developed lymphomatous tumors only.

4. The early incidence of fowl paralysis points to transmission through the egg.

5. The first case of paralysis and lymphomatous tumor in the same chick was observed at 79 days, indicating that the period of "incubation" is similar.

6. There was a difference in the incidence of fowl paralysis and lymphomatous tumors in the two groups of chicks. This is interpreted to mean that there is an inherent difference in susceptibility and resistance to fowl paralysis and lymphomatous tumors.

Acknowledgment

The authors wish to acknowledge their gratitude to Dr. H. W. Hill, Head of the Department of Bacteriology, and Professor E. A. Lloyd, Head of the Department of Poultry Husbandry, for their invaluable advice and unfailing interest in the investigations of fowl paralysis.

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COMPARISON OF EFFICIENCY OF THE RAPID WHOLE BLOOD AGGLUTINATION TEST WITH THE SERUM AGGLUTINATION TEST FOR PULLORUM DISEASE[1]

By Jacob Biely[2] and William Roach[3]

Abstract

The results obtained with the rapid whole blood agglutination test for pullorum disease, applied in the field, agree closely with the results secured with the rapid serum agglutination test, applied in the laboratory.

The accuracy of the diagnosis was found to depend upon the training and experience of the technician. When the whole blood agglutination test was applied by inexperienced persons, the results obtained differed from the laboratory test by 12% as compared with a difference of 1.3% when the whole blood agglutination test was applied by an experienced technician.

The rapid whole blood agglutination test was found to lend itself very readily to practical application in the field. The extremely low cost makes feasible the application and repetition of the test on a large scale.

Since it is known from previous work that one agglutination test will not eliminate all carriers of pullorum disease, the rapid whole blood agglutination test should be applied several times a year until at least two successive negative tests are obtained on each bird of the flock.

The recently developed "rapid whole blood agglutination test" for the detection of pullorum disease has given variable results, when compared with those of the serum agglutination test. It therefore appeared to be worthwhile to undertake further work for the purpose of comparing the results of the rapid whole blood agglutination test for pullorum disease in the field with the results of the rapid serum agglutination test in the laboratory. The present series of experiments were designed to test also the influence of the personal factor on the diagnosis of pullorum disease by the rapid whole blood agglutination test in the field. The need for further work along this line is indicated by the literature, which is here briefly reviewed.

In 1929 Bunyea, Hall and Dorset (7) reported that they had developed a simplified agglutination test in which whole blood and a specially prepared antigen were used. Bunyea and Hall (6) made a comparative study of the rapid whole blood agglutination test and the tube agglutination test, and reported 87.6% agreement on six flocks. Eight per cent of the cases reacted to the simplified test but not to the tube test; 5% reacted to the tube test but not to the simplified test.

J. R. Beach and Michael (1), Brandly (4), Sawyer and Hamilton (11), and Broerman (5), did not consider the simplified test to be a satisfactory substitute for the serum agglutination test. Bleecker (3) concluded that in the hands of an experienced operator the whole blood agglutination test is fully as efficient as the tube agglutination test.

[1] *Manuscript received February 9, 1932.*
Contribution from the Departments of Bacteriology and Poultry Husbandry, University of British Columbia, Vancouver, Canada, with financial assistance from the National Research Council of Canada.

[2] *Research Assistant, Department of Poultry Husbandry, University of British Columbia.*
[3] *Fieldman.*

The whole blood agglutination test has met with the marked approval of German investigators, and was found on the whole to be as accurate as the serum agglutination test (9, 10, 13, 14).

Schaffer, Macdonald, Hall and Bunyea (12) developed an improved antigen for the whole blood agglutination test, which had advantages over the old one in that it was adequately preserved, and was deeply stained by means of crystal violet.

Coburn and Stafseth (8) improved the antigen for the whole blood agglutination test (by adding 0.5% phenol and gentian violet) and used standardized dropper pipettes for measuring antigen and blood.

Method of Conducting the Tests

The details of the technique of the rapid serum agglutination test and the interpretation of the results have been reported in a previous paper (2). For purposes of the present paper, it is sufficient to state that the antigen (four strains of *S. pullorum*) is adjusted to a turbidity fifty times greater than tube 0.75 of McFarland's nephelometer; 0.4 cc. of serum and 0.2 cc. of standardized antigen are used; readings are made after five minutes incubation at 37° C., with second readings after two to three minutes at room temperature.

The technique employed with the rapid whole blood method varied in certain details from that generally recommended. The use of a flat glass plate was found unsatisfactory on account of the rapid drying of the blood smears, the deposition of dust, and a certain awkwardness in mixing the blood and the antigen. Instead, two white porcelain spot plates, with twelve sunken wells, were used. These were kept covered with plain glass, to exclude dust. Each plate had a manufacturer's trade mark on one edge, which was kept for reference as a starting point.

In each well, a drop of antigen was placed with a dropper designed to deliver 0.05 cc. As the birds were bled, a drop of blood was taken direct from the wing with an inoculating needle, the loop of which, in accordance with the recommendations of Schaffer *et al* (12), was $\frac{3}{8}$ in. in diameter. The blood and the antigen were mixed with the inoculator, and the plate was rotated to ensure complete mixing. The loop was rinsed in dilute coal tar disinfectant and dried after each test. The plates were washed in a similar solution which was kept hot, then dried with a clean towel.

By the use of two spot plates it was possible to read each test as the third succeeding test was made. A watch was used to time the reactions. Usually two or three readings were made. The diagnoses were recorded as positive, suspicious or negative. Positive and suspicious reactors were removed from the flocks.

Leg band numbers were recorded in four rows of three numbers each, to conform to the position of the wells of the spot plates, the trade mark being kept on the left of the operator when mixing blood and antigen.

Two poultry crates were used, the 12 birds tested on one plate being placed in one crate, the birds being released and the reactors removed as the readings of each plate were completed. Thus only two sets of bands, of different colors, numbered from one to twelve, were required.

The blood was secured by pricking the ulnar vein with a sharp Bard Parker blade No. 11 at the point at which the vein passes over the juncture of the humerus and the radius-ulna. Usually, very little or practically no bleeding followed when the blood was taken at this point, whereas a considerable loss of blood often occurs if an incision is made in the ulnar vein nearer to the body, as in the case of collecting blood for the serum agglutination test. With the above technique, from 100 to 125 birds were tested in one hour.

Blood samples from each bird were sent to the laboratory for the rapid serum agglutination test, this blood being collected in the usual manner.

Antigens for the rapid whole blood method were secured from three sources: (1) through the courtesy of Dr. M. Dorset, Bureau of Animal Industry, U.S. Department of Agriculture, Washington, D.C.; (2) and (3), from two commercial firms.

Results

Some preliminary tests were made in the laboratory with the B.A.I. antigen before any work was done in the field. In order to secure some idea of the diagnostic value and the sensitivity of the stained antigen used for the rapid whole blood method, several hundred blood samples were tested in the laboratory by the usual rapid serum agglutination test, and the sera retested in the same manner with the stained antigen. At first, difficulties were experienced

TABLE I

COMPARATIVE WHOLE BLOOD AND RAPID SERUM AGGLUTINATION TESTS

Flock	Number of birds	Whole blood antigen			Rapid serum antigen			Total disagreement
		Positive	Suspicious	Negative	Positive	Suspicious	Negative	
1	91			91			91	0
2	55			55			55	0
3	78			78			78	0
4	100			100			100	0
5	127	5		122	5		122	0
6	118	2		116			118	2
7	100			100			100	0
8	288	19		269			288	19
8a	198	5		193			198	5
9	74	14		60			74	14
10	40	6	1	33	7	1	32	3
11	219	39		180	42	3	174	11
12	71	10	3	58	9	1	61	3
13	188	10		178	13		165	3
14	137			137			137	0
15	40			40			40	0
16	322			322			322	0
17	62	20		42	20	1	41	3
12a	168	50	2	116	52	1	115	4
13a	224	13		211	13		211	0
18	29			29			29	0
19	93	8		85	7		86	1
20	110	68		42	69		41	2
	2932	269	6	2657	237	7	2678	70

in interpreting the reactions secured with the stained antigen. However, after gaining some experience in reading the tests with the stained antigen, practically identical results were secured.

The preliminary evidence of these tests indicated that the rapid whole blood stained antigen was as sensitive as the rapid serum antigen used in this laboratory, and that experience is necessary for the proper interpretation of the reactions.

Table I shows the comparative results secured with the two methods from twenty flocks, involving 2932 birds. It will be seen that, with the exception of three flocks (8, 8a and 9), the rapid whole blood agglutination test agreed very closely with the rapid serum agglutination test. The last column in the table shows the total number of birds that gave a positive or suspicious reaction with the serum agglutination test and a negative reaction with the whole blood method, and *vice versa*. Seventy birds, or 2.3% out of 2932 tested, failed to agree. If we exclude the three flocks (8, 8a and 9) to which reference will be made later, only 28 out of 2932 tests, or 1.3%, failed to agree. It will be further seen that at the close of the investigation, because of the experience gained, there developed practically complete agreement in the diagnoses by the whole blood and rapid serum agglutination tests. Beginning with flocks Nos. 8, 8a and 9, a new antigen was used. Discrepancies occurred in the first three flocks tested with the substituted antigen, which was decidedly more sensitive and rapid than the first one used. After a certain amount of experience with the second antigen, a close agreement with laboratory diagnoses was secured, and this close agreement was maintained when a third antigen was introduced. The first and third antigens used in the field were those secured from commercial firms.

On the basis of the data presented in Table I, it may be concluded that the rapid whole blood agglutination test and the rapid serum agglutination test are of equal value in the diagnosis of pullorum disease.

Influence of the Personal Factor

In order to test the influence of the personal factor in the interpretation of the field results, antigen was sent to several persons interested in the rapid whole blood agglutination test, but without experience. Instructions in technique and interpretation of results were sent to each. When their field tests were completed, the corresponding blood sample was sent to the laboratory for comparative diagnosis.

The results of this comparative study are given in Table II. The data show that there was considerable disagreement between these field results and the laboratory results; in fact, from the diagnostic point of view these field results were worthless. The last column in Table II shows that 145, or 12%, out of 1201 tests failed to agree. This contrasts markedly with the practical agreement of the two tests when the field test was made by an experienced person.

One of the flocks included in Table II was later retested simultaneously by two fieldmen, and a very close agreement with the laboratory test was secured. This flock was No. 11 in Table I and No. 1 in Table II.

TABLE II

THE EFFECT OF THE PERSONAL FACTOR ON THE ACCURACY OF THE WHOLE BLOOD AGGLUTINATION TEST IN THE DIAGNOSIS OF PULLORUM DISEASE

Person	Flock	Number of birds	Whole blood antigen			Rapid serum antigen			Total disagreement
			Positive	Suspicious	Negative	Positive	Suspicious	Negative	
"A"	1	225		5	220	42		183	47
	2	112		4	108			112	4
	3	86		6	80			86	6
"B"	4	460	21	2	437			460	23
	5	193	28		165			193	28
	6	49	5		44			49	5
"C"	7	33	4	3	26	9	1	23	15
	8	30	14	3	13	3		27	16
"D"	9	13			13	1		12	1
		1201	72	23	1106	54	1	1145	145

Discussion

Data secured in this investigation show that 98.7% of agreement was secured in the diagnosis of pullorum disease by the rapid whole blood agglutination test and the rapid serum agglutination test. In order to get such close agreement it is necessary that the test be made by a trained and experienced person. It is interesting to note here that Bleecker (3) obtained 91.15% agreement with 2159 birds when tested by the whole blood and tube agglutination tests, most of the discrepancies having occurred with the first few flocks tested. At the close of the experiment Bleecker obtained almost identical results with the two tests.

In the case of two flocks involving 140 birds, the tube agglutination test was used in a dilution of 1 to 25. Seventy-one birds reacted positively with the whole blood antigen in the field, while 69 reacted positively with the tube agglutination test. It is apparent from this that the antigen for the whole blood agglutination test is very sensitive in detecting pullorum disease carriers.

The effects of lack of experience and training in interpreting the whole blood agglutination test are clearly demonstrated in Table II. It is obvious that in several of the flocks used in the investigation the errors might have resulted in the discarding of valuable breeders, while in others it might have resulted in leaving numerous diseased birds in breeding flocks.

The importance of experience in the interpretation of agglutination tests is further emphasized by a case in which, out of a flock of 700 to 800 birds, 140 were diagnosed as "positives" by the rapid serum agglutination test, applied by a commercial laboratory, while actually only 8 out of the 140 reacted positively when tested in two other laboratories by experienced technicians.

In the case of flocks 4 and 5, Table II, the reactors were re-bled and submitted to a commercial laboratory for retesting. In the case of flock 4 no positive reactors were reported, while in the case of flock 5, three birds were reported as suspicious. One of these was submitted for post-mortem examination; this bird did not show pullorum disease lesions.

Since the field test appears to be as accurate as the laboratory test in the diagnosis of pullorum disease, the advantages of the rapid whole blood agglutination test over the tube and agglutination serum tests are obvious. The rapid whole blood agglutination test lends itself very well to the control of pullorum disease, and therefore its use in the field is warranted.

The advantages may be stated briefly as follows: 1. There is no necessity to draw a quantity of blood from a bird, a single drop sufficing for the test. 2. Reactors can be removed from the flock as soon as the test is applied, which eliminates the necessity of going through the flock a second time in a search for the reactors, which is necessary with the other tests. 3. There is no need of a bird being permanently banded. 4. The test can be performed at any time of the year. 5. By means of repeated testing pullorum disease could be eradicated in one season. 6. No expensive equipment is required, hence the cost is relatively low.

Acknowledgment

The writers wish to thank Messrs. M. H. Ruttledge and T. J. Smith, President and Managing Director respectively, of the R.O.P. Poultry Breeders' Association of British Columbia, and Mr. W. J. Spence of the Canadian Hatcheries Limited, for their deep interest in this work and their ready assistance in providing flocks for making the double test. They wish to express also their appreciation to Dean F. M. Clement of the Faculty of Agriculture, University of British Columbia, for making a special grant to conduct this investigation, and to Dr. H. W. Hill for permission to use the facilities of the Department of Bacteriology.

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PHENOMENA OF PRIMENESS[1]

By Charles Kenneth Gunn[2]

Abstract

The condition of muskrat pelts known as "primeness" is found to be independent of dermal characteristics and to be a function of epidermal pigment distribution. The microscopic characteristics of prime and unprime fur pelts are discussed and correlated with the macroscopic characteristics. A method is suggested for detecting primeness in the skin of living animals.

Introduction

The characteristics of a pelt which determine its value as a "fur" are certain variable characters of the epidermis—the so-called pelage—and of the dermis—the so-called leather.

Two characteristics in particular are of primary commercial importance, those of thickness and primeness. Such factors as the color, uniformity, sheen, length and density of the pelage, are subsidiary to the characteristics of dermal thickness, and of epidermal and dermal primeness. Upon dermal thickness depends the success of the technical processes of dyeing and dressing, and the durability of the finished product. Upon primeness depends the color, sheen, length and density of the pelage and the pigmentation of the leather.

An exact knowledge as to what constitutes "primeness", which in the last analysis is the ultimate criterion of the pelt, is therefore of fundamental importance. The existing methods of estimating primeness are empirical, do not take into account the morphological and physiological factors which underlie this condition, nor can they be applied to living animals.

The aims of this investigation therefore were:—

(1) To ascertain the histological differences between prime and unprime pelts.
(2) To correlate seasonal changes in the pelt with the visible phenomena of moulting and the growth of new fur.
(3) To provide a method for the separation of prime from unprime pelts, based upon such histological differences that can be applied to the pelts of *living* fur-bearing animals.

Methods

The material consisted of living male muskrats (*Fiber zibethicus albus*) from Washow Bay, on the west coast of Lake Winnipeg, and a large number of treated and untreated pelts. Male animals were used to avoid any variations in the pelt which might result from secondary effects caused by oestrous periods. One rat pelted on September 26, showed marked unprimeness along the mid-dorsal region; from these unprime pigmented areas microscopic sections were made. Sections of a prime pelt were prepared from a muskrat, from the same ranch, pelted on February 1.

The microtechnical procedure consisted of Bouin fixation, followed by haematoxylin, eosin or picro-fuchsin stains.

[1] *Manuscript received May 16, 1931.*
Contribution from the University of Manitoba.
[2] *Demonstrator in Zoology, University of Manitoba.*

Structure of the Pelt

By shearing the fur and carefully stripping the panniculus carnosus muscle from the untreated dried pelt, it is possible to examine and study the remaining portion of the leather directly with the low power of the microscope.

In such preparations the field is seen to be strewn with irregular groups and rows of densely pigmented hair roots, embedded in a flesh-colored connective tissue (Text–fig. 1). The hair roots are of two kinds. A large type, the guard-hair roots, are scattered sparsely over the field; their pigment is diffusely distributed in the bulbous portion of their roots: a much smaller, but more numerous type, the underfur hair roots, are arranged in groups, either around

TEXT-FIG. 1. *Diagram showing the arrangement of hair roots at the junction of prime and unprime areas of muskrat pelt.*

the larger roots of the guard-hairs or in clusters and rows without a central guard-hair, and with the melanin granules so densely concentrated in the ampulla of the root as to give the root the appearance of a black wedge-shaped structure.

From the outer end of this wedge small blocks of pigment pass from the adjoining portion of the root, at first closely packed together, but becoming more definitely separated from each other, as they pass into the portion of the hair root nearer to the mouth of the follicle. In the roots of the underfur hairs, the melanin is confined completely to the medulla, while in the case of the guard-hairs it also permeates the cortex and is not distributed in a block formation.

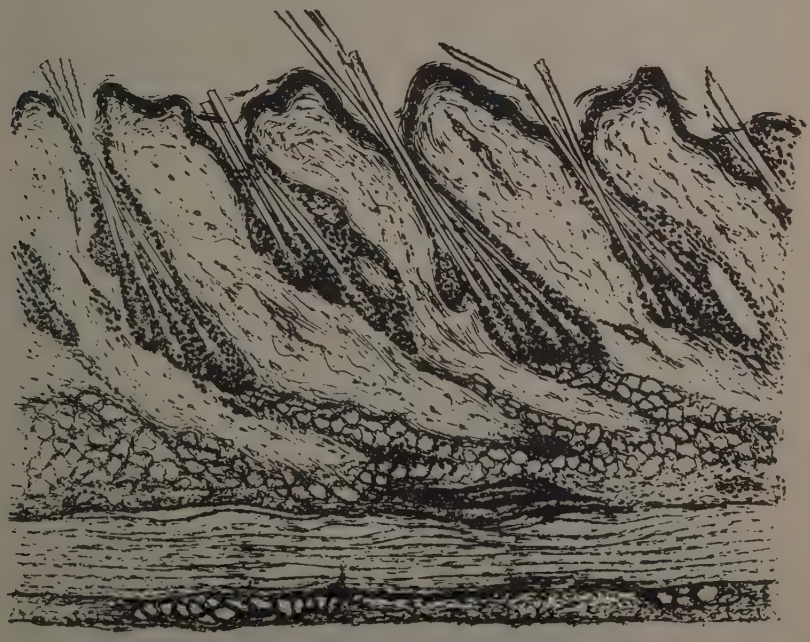
A similar preparation of a prime area shows no hair roots, but only the connective tissue ground substance (Text-fig. 1). The roots are not hidden by an external layer of fibrous tissue, but are invisible because they are completely devoid of melanin.

The blue coloration of the inner layer of the unprime skin which is commonly accepted in the fur trade as indicating unprimeness, is in fact, the massed effect of the pigmented roots. The pink, fleshy color of the prime skin is due to the absence of pigmentation in the hair roots.

It is possible for a muskrat pelt to be as thin as paper, but to be fully prime, and for the skin to be approximately $\frac{1}{8}$ in. in thickness in certain pelts and yet be markedly unprime.

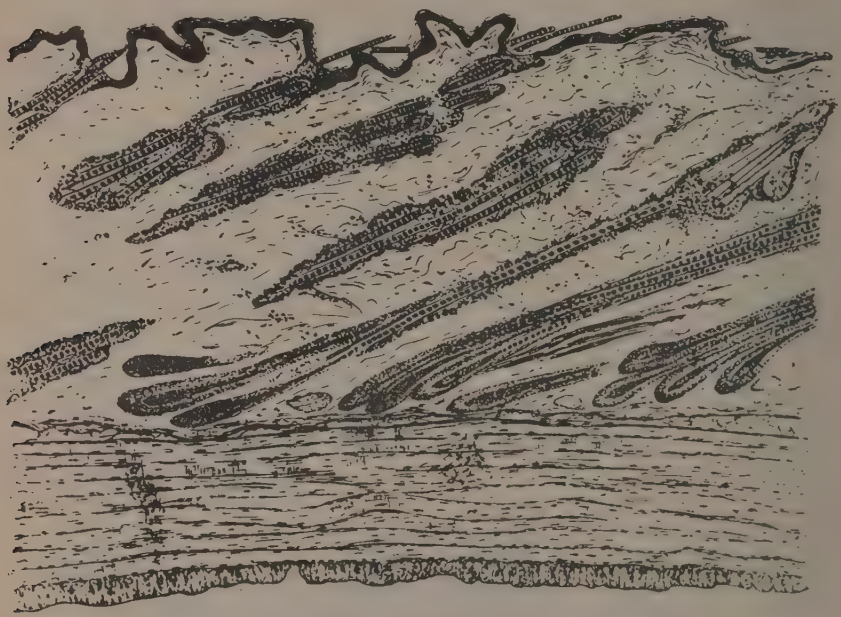
That is to say, primeness or unprimeness is not dependent upon the thickness of the dermis. It is not, as is commonly understood, a pigmented condition of the dermis, but of the pelage, and is due to difference in the distribution of the melanin within the proximal portion of the hairs and their roots.

If vertical sections of a portion of prime skin be examined (Text-fig. 2), the skin is seen to be composed of a relatively thin layer of epidermis, below which lies a thick dermal layer containing the hair roots and follicles with sebaceous glands and arrector pili muscles. Beneath the skin are found the longitudinal muscle fibres of the panniculus carnosus muscle, which is attached by a thin



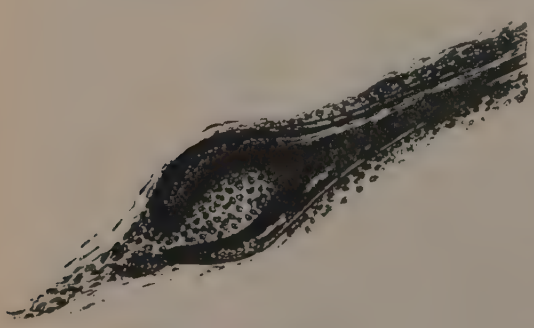
TEXT-FIG. 2. *Transverse section of prime muskrat skin.* × 55.

layer of fascia to the body musculature. This muscle, although an important constituent of the pelt, is not a "skin muscle" but is a derivative of the pectoral musculature, and is innervated by the nn. thoracales anterior branches of the brachial plexus (7).



TEXT-FIG. 3. *Transverse section of unprime muskrat skin.* × 55.

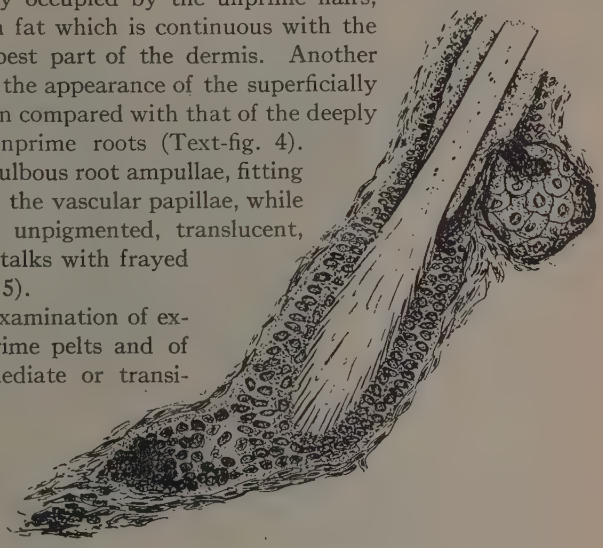
Sections of unprime skin show several remarkable differences from the prime condition, particularly with regard to the pigmentation of the hair roots, the relative position, angle and depth of the hairs in the dermis, and the appearance of the root-bulbs in relation to the root papillae.



TEXT-FIG. 4. *Guard-hair root from an unprime area of skin.* × 160.

An important difference between prime and unprime skins concerns the relative depth of the hair roots in the dermis. The unprime or pigmented roots originate in the deepest part of the dermis and are arranged at a very acute angle to the skin surface (Text-fig. 3). In the fully prime pelt the hair roots are situated in the outer half of the dermis and are almost vertical

(Text-fig. 2). Below these groups of prime hairs, trains of follicular cavities are seen curving up from the deeper part of the dermis, from a more horizontal plane than that now assumed by the prime hairs. These cavities, from all evidence, were formerly occupied by the unprime hairs, but are now filled with fat which is continuous with the fatty layer in the deepest part of the dermis. Another noticeable difference is the appearance of the superficially placed prime roots when compared with that of the deeply situated, pigmented unprime roots (Text-fig. 4). The latter have more bulbous root ampullae, fitting like inverted cups over the vascular papillae, while the former appear as unpigmented, translucent, very slightly bulbed stalks with frayed extremities (Text–fig. 5).



TEXT-FIG. 5. *Guard-hair root from a prime area of skin.* × *160.*

From an extensive examination of extreme prime and unprime pelts and of sections of the intermediate or transitional stages of primeness, the conclusion may be drawn that the differences represent merely different phases in the life cycle of the hair. The very young hair has a bulbous root, densely pigmented and situated in the deepest portion of the dermis. The pigment is continued out into the young hair as a continuous core which is often seen to end in a tapering point. Frequently the bulbous part of the root makes a sharp loop or is angled at its junction with the remaining portion of the root, which may be due to the young hair following the old follicular cavity or path of least resistance (Plate II, 1).

As this hair grows older the pigment becomes less dense and assumes a granular appearance, and often shows irregular distribution at the basal extremity. Later the root appears to undergo a process of absorption and atrophy in the region just above the papilla and to assume a depigmented, hyaline appearance throughout, as well as shrinking in diameter. Meanwhile the root is migrating outwards, devoid of an ampulla, and pulled away from the papilla, which remains in the deeper part of the dermis surrounded by a remnant of epithelial cells, from which the next hair generation will probably arise.

This maturation or priming process, although it brings about a separation of the hair root from the papilla, does not sever the hair from all vital connection, however, for when such hairs are clipped from the body of an animal which exhibits seasonal color change, this process is discontinued.

Another structure which may play an important role in bringing about the outward migration and assumption of a more vertical position in the group of

hairs when they become prime, is the arrector pili muscle, which in a few sections is seen attached to the base of the follicle of a group of hairs in its new position. The slightly bulbed prime roots are surrounded by individual epithelial follicles at their deeper extremities, but the outer portions of the roots are more compactly wedged into a common follicle surrounded by a definite connective tissue sheath. Owing to this mechanical arrangement, any outward strain on the hairs of the prime pelt only tends to wedge them more firmly.

The Relation of Unprimeness to Moulting

The pelt of the muskrat consists of two kinds of hairs; a soft thick hair comprising the under-fur, and a longer stouter hair, the guard-hairs, or the protective hair, which overlies the under-fur and, as its name implies, protects and also prevents matting of the under-fur.

An examination of the fleshy side of an *autumn pelt*, taken about October 1, will show the ventral and ventro-lateral regions to be prime, but there may be large blue unprime areas in the region of the neck, around the root of the tail and scattered irregularly along the dorso-lateral areas. On examining the fur, the guard-hairs will be found to be plentiful and the under-fur will be dense in the ventral region of the pelt, but on the dorsal region, the guard-hairs may appear relatively long, owing to the fact that the under-fur here has not attained its full length.

A fully *prime pelt*, taken in the latter part of March, while at the peak of primeness, shows the optimum conditions of sheen, color, texture and density of the fur, and on the fleshy side is devoid of pigmentation. This is the period when the pelt is at the apex of condition and from this time on it usually declines in color, sheen, and so forth.

A *spring pelt* shows the initial stages of moulting. Here the guard-hairs are beginning to shed, especially from the ventral region. The fleshy surface however shows no sign as yet of pigmentation, but does show a marked change in color from a bloody or fleshy color as seen in autumn or winter, to a whitish color. This is due to a decreased vascularity and a deposition of fat on the dermal and fascial sides of the panniculus carnosus muscle.

Pelts taken in the early summer show a slight amount of matting of the under-fur, especially where the old guard-hairs have completely disappeared, and where the young ingrowing guard-hairs are not as yet very long. The under-fur constitutes the main portion of the coat of the animal at the season when the guard-hairs are noticeably absent. But here there is also evidence of early moulting of the under-fur in the ventral regions. The fleshy side of the pelt at this season shows a dense pigmentation owing to the presence of heavy deposits of melanin in the roots of the young ingrowing hairs. The pigmentation at this time is most dense in the ventral region and least dense along the mid-dorsal line, owing to the ingrowth of young under-fur hairs, and of guard-hairs, reaching the maximum concentration first in the ventral portions of the pelt (Plate I, 1).

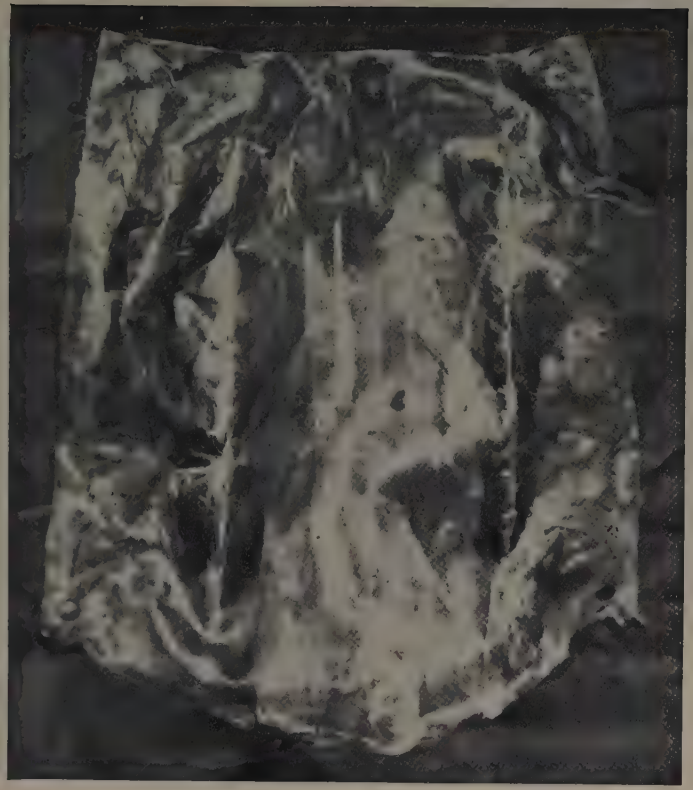
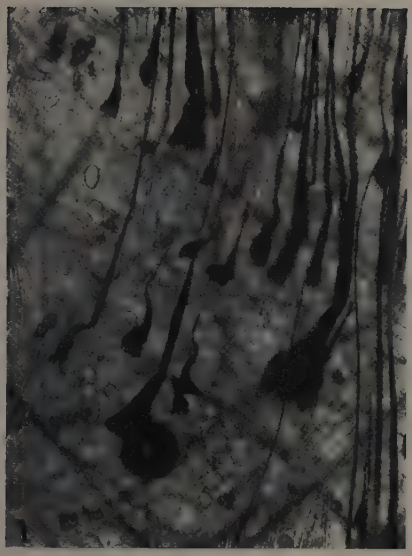
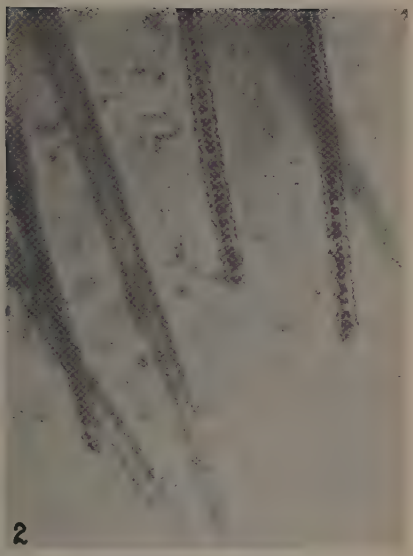


FIG. 1. *Summer pelt showing mid-dorsal area prime, i.e., converse to winter pelt.*

FIG. 2. *Weasel pelt in final stages of blanching process.*

PLATE I





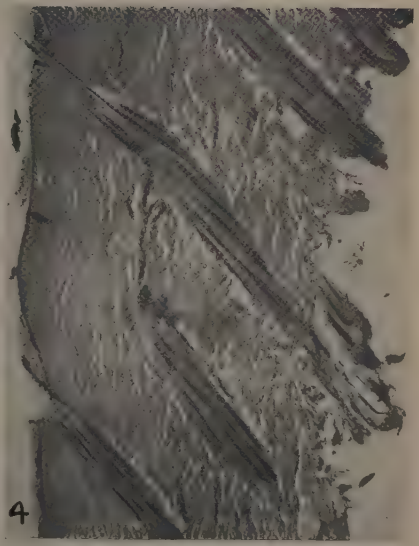


FIG. 1. *Microphotograph of unprime pelt.* ×78. FIG. 2. *Microphotograph of proximal ends of underfur hairs from an unprime area of pelt.* ×375. FIG. 3. *Microphotograph of proximal ends of underfur hairs from a prime area of pelt.* ×375. FIG. 4. *Microphotograph of transverse section of skunk pelt, without panniculus carnosus muscle.* ×16.

An examination of pelts taken later in the summer shows evidence of moulting as before, but not in the same regions. Now, the shedding process is confined more to the sides and back of the animal and affects the under-fur of these regions. In the ventral regions the young guard-hairs are in evidence and also the short under-fur of the new coat.

In conclusion, to summarize the information available concerning the relation between moulting and unprimeness, and the new growth of fur, it is quite evident that the shedding process does not take place simultaneously in the guard-hairs and under-fur, nor does it occur uniformly throughout the different regions of the surface of the body, but takes place over the various body areas at different intervals of the moulting season and follows a definite sequence, namely:—

(1) First the guard-hairs are shed from the ventral regions of the body surface, and then the under-fur. This process, in this order, then spreads to the lateral and finally into the dorsal surfaces of the trunk of the animal.

(2) First to appear in the new coat are the guard-hairs in the ventral region, then the under-fur. Thus it is evident that the ingrowth of the new coat follows the sequence of the moult.

The last place to become fully furred is the dorsal portion of the body surface and here first the guard-hairs and later the under-fur grow into the new coat. Thus the animal has an adequate coat of fur and at no time is completely devoid of protection, whether it be from the rigors of winter or the heat and actinic rays of summer.

Seasonal Changes in the Appearance of the Leather

The seasonal changes in the character of the fleshy side of a pelt vary according to the time of the year in which the animal is pelted. The fleshy side of an autumn and winter pelt is red in color owing to the presence of a copious blood supply to the panniculus carnosus muscle and underlying connective tissue, but the fleshy appearance gives place to a blue-black pigmentation, limited to several large well-defined unprime areas in the lateral and dorsal regions, especially evident in the skin from the back of the neck along the mid-dorsal line and above the root of the tail. These are the last areas to become prime and may even show evidence of pigmentation in late winter muskrat pelts, but usually they have reached the prime state by the end of March or April.

When animals are trapped in the late spring of the year, the color of the inner surface of the pelt is seen to be changing from red to white, owing to the diminishing blood supply to the pelt, and to the deposition of fat in the skin. Although the guard-hairs at this season pull out more easily, there is as yet no sign of pigmentation in the dermis. Later in the spring the pelt becomes dark red and feels thick, greasy and board-like on the leather side when cased, and the fur is found to be scanty in amount. This kind of a pelt is known in the fur trade as "springy".

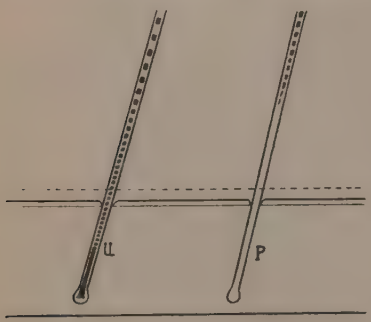
Finally, if pelts taken in mid-summer are examined, they are found to be blue on the ventral surface owing to the very dense pigmentation of the roots in the new ingrowing young hairs. At this season the densest pigmentation is seen in the ventral areas of the pelt. The initial stages of pigmentation are seen in the shoulder areas, thence extending posteriorly along the ventro-lateral aspects of the thorax, abdomen and covering the perineum (Plate I, 1). At a slightly later period of the summer this black coloration is visible on the sides and back on the body surface, but unlike the autumn condition, the pigmentation is speckled over this region.

Thus the value of a pelt may be judged by the color of the inner surface, since this is merely an expression of the phenomena taking place in the fur and therefore is indicative of its condition.

The Detection of Primeness or Unprimeness in the Living Animal

The principle of this test is based upon facts obtained by microscopic study of prime and unprime sections. The different areas of the skin surface of an animal, however, become prime at different times of the year and remain at the peak of condition over a short period of the season. The order of priming in a pelt is as follows:— (1) the ventral regions; (2) the lateral regions; (3) the dorsal regions.

The last portions of the dorsal area to become prime are those at the back of the neck and just anterior to the root of the tail. It has been pointed out that the guard-hairs in the new coat appear first and the under-fur comes later, so that the last fur in the muskrat to become prime is the under-fur of these dorsal regions.



TEXT-FIG. 6. *Diagram showing distribution of pigment in (P) prime and (U) unprime hairs.*

A study of vertical sections, and especially of the hair side of the pelt, with a binocular microscope will show that depigmentation of the hair roots does not stop at the level of the epidermis, but is continued out into the hair to a variable extent in different animals (Text-fig. 6). If the hair be examined a short distance out from the epidermis the pigment is seen to return, at first in small irregular groups of melanin granules in the medulla, but which soon assume the characteristically blocked arrangement common to the outer portions of all the under-fur hairs.

The detection of prime from unprime portions of a pelt therefore simply requires the microscopic examination of samples of under-fur hairs cut close to the skin, and an examination particularly of the root ends of these. The hair from the unprime pelt (Plate II, 2) shows pigmentation of a heavy blocked type (discontinuous medulla) extending down to the cut end, while

the hair from a prime pelt shows as a clear hyaline structure, devoid of pigmentation for a variable distance from the cut end (Plate II, 3). The difference is very obvious in hairs derived from prime and unprime areas of a pelt.

The distribution of the pigment thus serves as an exact external indicator of the condition of the skin in estimating the relative primeness of different animals which may show wide variation in time of reaching the peak of this condition, owing to age, sickness, or other natural causes. The test is applicable to a wide range of fur-bearing animals with the exception of albinos, but probably lends itself to more practical application in the fox ranching industry.

Practical Application

The animal is held whilst the fur at the back of the neck is wetted and parted. Then, by means of a straight-edge razor a small lock of under-fur is shaved off close to the skin. The lock is picked up by forceps just behind the former point of attachment to the skin and the outer portion is twisted in order to hold the root-ends together. This facilitates their examination in the dry state under the low power of the microscope. A sample which shows all the root-ends devoid of pigmentation indicates primeness, while the presence of pigmented root-ends even among prime hairs means that the skin from which they originated is not fully prime. This procedure is then repeated with samples taken along the mid-dorsal line and from the region anterior to the root of the tail. Then from the study of the sequence of primeness it is evident that if the samples taken from these areas are prime, the rest of the pelt is already prime.

Discussion

It is evident, from an histological examination of pelts taken from the animal at different seasons of the year, that many features such as unprimeness or pigmentation in the leather, lack of pigmentation of prime pelts, shedding of the fur, etc., are merely the outward expression of changes taking place in the hair and its root during the different phases of the life cycle. Pigmentation is present in the actively growing young hairs which are in direct communication with the vascular papillae, whilst primeness is associated with depigmentation in the root and hair shaft, in the latter to a variable distance in different animals, save in albinos (4). This blanching process is probably seen in its most exaggerated form in such animals as the varying hare, jack rabbit, weasel and arctic white fox, in which it would appear that primeness means, not only depigmentation of the root and proximal part of the hair, but also of the outer hair shaft. This view would account for most of the facts put forward in a recent paper on color change in *Lepus americanus* (5) which asserts that: "Probably the most convincing proof that the change takes place in existing hairs is to be found in the skin itself when the hair roots are examined. The fact that the roots cease to function as the hair turns white, and that it is a progressive change, offers conclusive evidence that the alteration is destructive."

There are objections to this view that seasonal color change in rabbits, etc., is due to a depigmentation process in the roots, since it is evident from the

study of primeness in other colored fur-bearing animals, such as the muskrat, that the roots here also become depigmented when the prime state is reached, without the outer fur blanching. It may be suggested in fact that the seasonal depigmentation, with the consequent color change is merely an exaggerated state of a priming process which occurs annually in all fur-bearing animals, to a variable but lesser extent (excluding albinos). Further evidence supporting this view is found in the fact that the sequence followed in the priming and blanching processes is the same. Thus, not only are the areas at the back of the neck and root of the tail the last to become prime, but also to change color, in variable animals (Plate I, 2).

The impression that the hairs pull out more easily from an unprime pelt than from a prime pelt is a mistaken interpretation of the facts, although it is stated thus by fur-dressers. From the study of the relation of shedding to unprimeness in pelts it is evident that young or pigmented hairs are present where shedding is in progress, and it has been wrongly supposed that these are the hairs which shed more readily. As a matter of fact, as shown by sections of unprime skin, these hairs are more deeply embedded in the dermis and exhibit a definite ampulla firmly attached to the root papilla which anchors them even more firmly in the skin than the prime hairs, which have partly lost this attachment. The hairs which pull out more easily represent a remnant of the former coat which is in the process of shedding in this unprime area.

Another defect which cannot wholly be attributed to unprimeness is that, when unprime pelts have passed through the tanning and dressing processes, the hairs often project on the fleshy side of the leather. This may be the result of improper handling.

In the scraping, the carnosus muscle may be detached from the skin and partly or wholly removed; then, since the hair roots are embedded in the deeper part of the dermis in an unprime pelt, and the tanning process removes the fat in the deepest layer from around the roots, they become exposed and project through the inner surface of the leather (Plate II, 4).

Another cause of this condition is the "fleshing" process. Since the hair roots are so near the inner surface of the leather in the unprime pelt, they may be cut off during this process and owing to the serrate edges of the hair cuticle which project towards the external surface, the hairs tend to work towards the inner side of the leather, when the pelt is subjected to the further manipulation necessary in the dressing process.

In view of the great importance attributed to primeness not only in the grading of furs from the aspect of their consequent money value, beauty and durability, but from the stress laid upon this condition in the legal interpretation of the Game Act, a clear and definite standard of what constitutes primeness and unprimeness is of due importance.

The test for primeness permits the use of the hair shaft as an external indicator of the invisible underlying changes taking place in the skin of the *living* animal, not only as an indicator of the prime condition, but of the influence of varied diets in the production of optimal coloration and their forcing or retarding effect upon the onset of primeness.

Acknowledgments

The author wishes to acknowledge his indebtedness to Messrs. E. Chevrier, A. Lanthier, P. Robinson, Bliss and Cohn, and the A. B. Shubert Fur Company, for materials, and especially to Prof. R. A. Wardle, under whose supervision the work was done.

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STUDIES OF POLYMERS AND OF POLYMERIZATION.

VI. THE VULCANIZATION OF METHYL RUBBER[1]

By George Stafford Whitby[2] and Morris Katz[3]

Abstract

Samples of synthetic rubber prepared by the polymerization of dimethylbutadiene at room temperature and at 45° C. respectively were subjected to vulcanization tests in comparison with natural rubber. In an accelerated gum stock containing 3% sulphur the cold polymer gave at best vulcanized products less than one-third as strong and only about one-third as extensible as natural rubber; the heat polymer gave products as extensible but only one-tenth as strong as natural rubber. The incorporation of carbon black greatly increased the strength of the synthetic rubbers, rendering both about half as strong as natural rubber in a similar stock. The vulcanized synthetic rubbers were less "snappy" than natural rubber at room temperature. Increase of temperature improved their speed of retraction, but seriously reduced their breaking strength. Products from the cold polymer showed a greatly increased stiffness and strength at 5° C. as compared with room temperature, and at about 1° C. were non-retractible. In general the synthetic rubbers were much more sensitive than natural rubber to change of temperature. A 50:50 mixture of the heat and cold polymers was also subjected to tests.

The ability of 2, 3-dimethylbutadiene to undergo polymerization to a rubber-like product was first observed by Kondakov (8). When, during the war, the manufacture of synthetic rubber on a large scale was, owing to the exigencies of the time, undertaken in Germany, the polymerizant chosen was 2, 3-dimethylbutadiene, and, since this is a methyl homologue of isoprene, the polymerizant of natural rubber, the rubber produced was designated methyl rubber. About 2350 tons of methyl rubber was manufactured at Leverkusen during the war, and at the close of the war there was in course of erection two additional plants for its manufacture with a joint capacity of 8000 tons a year (4 p. 214, 6). Accounts of the German wartime experience with methyl rubber have been given by Gottlob (5), Duisberg (3), F. Hofmann (6), Burgdorf (1) and Weil (10), but the descriptions of the properties of methyl rubber given by these writers are in general terms only, and, with the exception of Pohle's work on the colloidal behavior of this rubber (9), there is in the literature a lack of any numerical or other exact data concerning the properties of methyl rubber, especially after vulcanization, which would enable them to be compared in quantitative terms with the properties of natural rubber. In view of this lack and of the renewed interest in synthetic rubber which has been excited by the discovery of a synthetic rubber from 2-chlorobutadiene (2) the present work was carried out.

In an earlier paper of this series data have been given on the rate of polymerization of dimethylbutadiene under the influence of heat and on the molecular weight and viscosity of the resulting methyl rubber (12). In the present paper are recorded experiments on the vulcanization of methyl rubber and the properties of the vulcanized products as compared with the properties

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Contribution from the National Research Laboratories, Ottawa.

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of vulcanized natural rubber. The experiments were confined to soft vulcanized rubber, partly because the statements in the literature relating to the German wartime experience are more definite in regard to the preparation of hard, than in regard to the preparation of soft, rubber from methyl rubber, and partly because the amount of material available was limited. There was used in the experiments methyl rubber of two types, namely (*a*) rubber formed by spontaneous polymerization at room temperature; (*b*) by polymerization at 45° C. These are referred to as the cold polymer and heat polymer respectively and may be compared roughly with the *H* (hart) and *W* (weich) rubbers formerly manufactured in Germany by polymerization at 30° and 70° C. respectively.

In the experiments carried out, the methyl rubbers obtained by cold and by hot polymerization and also a 50:50 mixture of these products were compared with natural rubber in a gum stock and in a carbon black stock. The influence of temperature on the tensile strength, elongation and retractive power of the vulcanizates was also studied.

It was found that in a gum stock the cold polymer gave, at the best cures, vulcanized products less than one-third and the heat polymer not more than one-tenth as strong as were given by natural rubber. The vulcanized cold polymer suffered rupture at a low elongation, the ultimate extension being only about one-third that of natural rubber. The vulcanized heat polymer on the other hand, although, as already stated, far weaker than vulcanized natural rubber, was almost as extensible as the latter (see Table I).

The incorporation of carbon black exercised a much more striking effect in methyl than in natural rubber, particularly in the case of the heat polymer. The addition of 25 parts of this ingredient to the gum stock raised the maximum tensile strength from 28.2 to 166.5 kg. per sq. cm. in the case of the heat polymer; from 86.4 to 161 kg. per sq. cm. in the case of the cold polymer, and only from 293 to 349 kg. per sq. cm. in the case of natural rubber. The profound effect of carbon black on the tensile properties of methyl rubber is shown, not only by the increase in the ultimate tensile strength just noted, but also by the marked stiffening of the stock. The cold polymer, already somewhat stiffer than natural rubber in the gum stock, was, by the addition of carbon black, rendered far stiffer than natural rubber in a similar stock, the load required to extend to twice the original length samples cured to the point of maximum tensile strength being 54.2 and 19.7 kg. per sq. cm. in the two cases respectively (see Table I). Increase in the carbon black from 25 to 50 parts did not, in experiments with the cold polymer, further increase the ultimate tensile strength, although it stiffened the rubber compound, as is indicated in Table I by the figures for T_2 (load producing an extension of twice the initial length). The effect of carbon black in raising the tensile strength of synthetic rubber has lately been mentioned in the patent literature (7).

In view of the relatively small influence of carbon black on natural rubber as compared with its great effect on the soft, heat polymer, it may be surmised that in natural rubber only a very small fraction if any of it is soft material in a relatively low state of polymerization.

As other papers (13, 14) in this series show, high polymeric products are in general markedly heterogeneous and consist of mixtures of polymeric molecules representing a range of molecular weights. Methyl rubber produced by heat polymerization was shown to be thus heterogeneous (12), and it seems fair to assume that the cold polymer too is heterogeneous. Further, it has been shown that, other things being equal, the lower the temperature at which the polymerization of a given polymerizant occurs, the higher is the mean molecular weight of the polymerizate. Hence it is probable that methyl rubber produced by polymerization at room temperature ("the cold polymer") has a higher molecular weight than methyl rubber produced by polymerization at 45° C. ("the heat polymer"). The behavior of the two materials towards solvents and swelling agents, as recorded in the experimental part, is in accord with this view. The heat polymer disperses much more readily than the cold polymer; indeed the latter failed to disperse in all the liquids employed and it was in consequence impossible to determine its molecular weight.

In the case of polystyrene it has been established (15) that the elastic properties of samples prepared in different ways depend on the molecular weight. Material obtained by the spontaneous polymerization of styrene at room temperature has a much higher molecular weight than material obtained by polymerization at *e.g.*, 140° C., and, correspondingly, disperses less readily in solvents and has different elastic properties. The cold-polymerized material has a greater strength and smaller extensibility than the heat-polymerized material. This is analogous to the behavior of the vulcanized products from the samples of methyl rubber obtained in the cold and at an elevated temperature.

It may provisionally be considered that in order to secure optimum elastic properties in an elastic polymer, *i.e.*, high tensile strength together with high extensibility, it is necessary that the polymeric molecules present shall extend over a certain optimum range and shall be present in appropriate proportions. In order to secure stress-strain relations similar to those exhibited by natural rubber, it would seem that, speaking broadly, there should be present a suitable proportion of material in a relatively low state of polymerization in order to render the material readily extensible on the application of small loads; a suitable proportion in an intermediate state of polymerization and responsible largely for the intermediate part of the stress-strain curve, and a suitable proportion in a high state of polymerization which confers tenacity, enables high loads to be sustained with little deformation and is responsible largely for the last part of the stress-strain curve.

In view of considerations such as the foregoing, experiments were carried out on the vulcanization of a mixture of equal parts of the cold and heat polymers. The former polymer, representing material in a higher state of polymerization, yields on vulcanization alone a product of relatively good strength but poor extensibility; the latter, representing material in a lower state of polymerization, a product of poor strength but good extensibility. The product from the 50:50 mixture was found to have almost as good an extensibility as the heat polymer alone and a tensile strength between that of the heat and cold polymer.

The amount of material available did not permit of experiments on mixtures in other proportions, but such further experiments would probably be instructive and are to be desired.

The vulcanized products from methyl rubber not only had a markedly lower tensile strength than those from natural rubber but much poorer "nerve"; that is to say, when allowed to recover under no-load after being extended, they retracted with much less "snap" than natural rubber. This was particularly so with the cold polymer, which retracted very sluggishly and was decidedly loggy. The figures for "set" given in Table I represent the residual extension in per cent half an hour after the specimens had been stretched to the point of rupture. These figures do not well reveal the lack of "snap" in the synthetic rubber. The latter is however well shown by the figures given in Table II for the residual set left at intervals up to four minutes after stretching specimens to 150% and then allowing them to retract under no-load. It was observed that when warmed the specimens of methyl rubber largely lost their sluggishness. This is shown by the data given in Table II on the retraction of the specimens when allowed to retract at 45° C. after being stretched 150% at that temperature. At 70° C. the samples of vulcanized methyl rubber retracted with almost as good a "snap" as natural rubber, but, as data in Table III show, were lacking in strength.

The effect of introducing small proportions of plasticizers into the stiff, carbon black stock from the cold polymer was examined. It was found to increase somewhat the ultimate extension (Table I) and to improve, but not strikingly, the speed of retraction (Table II).

The tensile properties of methyl rubber vulcanizates were determined not only at room temperature, but also at a reduced temperature (5° C.) and at elevated temperatures (37° and 70° C.). (See Table III.) It was found that all the specimens of vulcanized methyl rubber were much more sensitive to temperature changes than was natural rubber. The heat polymer was particularly sensitive to fall of temperature and the cold polymer to rise of temperature. Reduction in the temperature from 20° to 5° C. increased the tensile strength of the gum vulcanizate from the cold polymer from 28.2 to 181 kg. per sq. cm. Increase in the temperature from 20° to 37° C. reduced the tensile strength of the gum vulcanizate from the heat polymer from 68.4 to 10.9 kg. per sq. cm. Natural rubber on the other hand showed little stiffening when the temperature was lowered to 5° C. and relatively little softening when it was raised to 37° C., the figures for tensile strength at 20°, 5° and 37° C. being 285, 272 and 219 kg. per sq. cm. respectively. Even at 70° C. the natural rubber retained a substantial amount of its tensile strength, especially when it was compounded with carbon black, whereas methyl rubber was extremely weak. Thus, for example, the gum polymerizate from the cold polymer, which at 20° C. had a tensile strength of 68.4 had at 70° C. a tensile strength of only 2.4 kg. per sq. cm.

In conclusion it may be remarked that methyl rubber is certainly susceptible to being influenced in its rate of vulcanization by an accelerator such as is effective with natural rubber. Several attempts to vulcanize a simple mixture

of 100 parts methyl rubber (cold polymer), 5 parts sulphur and 5 parts zinc oxide at 133° C. were entirely unsuccessful. The mixture was quite uncured and stuck to the mould after seven hours' heating. On the other hand, as the data in Table I show, a mixture of the rubber containing only three parts of sulphur but in addition one part of an accelerator of the dithiocarbamate class was well vulcanized after 30 min. heating at 110° C. It may be noted further that the methyl rubbers are much less susceptible to overcuring than is natural rubber. Thus, for example, in the gum stock used natural rubber is well cured in 15 min. at 110° C. and overcured in 20 min. or less at 133° C., whereas methyl rubber (cold polymer) gives similar results on the one hand in 30 min. at 110° C. and on the other hand in 80 min. at 133° C.

Gottlob (5) has stated that in the early experiments with methyl rubber it was found that vulcanization in the presence of sulphur and fillers only led to combination of not more than a few tenths per cent of sulphur, but when heated with 10% of sulphur for one hour at 152.4° C. (4 atm. steam pressure) in the presence of piperidine "a few per cent of sulphur were combined". In the present experiments on the vulcanization of methyl rubber in a stock containing a very strong accelerator combination, *viz.*, a dithiocarbamate with zinc oxide, it was found that the rate of combination of sulphur was of the same order of magnitude as, albeit a little slower than, with natural rubber, and that the heat polymer combined with sulphur a little more slowly than the cold polymer. Data are given in Table V.

Vulcanized methyl rubber was found to imbibe swelling agents to a similar extent to natural rubber (Table IV).

Experimental

The methyl rubber used in these experiments was obtained as follows. Dimethylbutadiene was heated in sealed glass tubes at 45° C. for 186 days. This caused the polymerization of a part of the diene and yielded a viscous liquid. The contents of the tubes were then allowed to stand at room temperature for four summer months, and when the tubes were then examined it appeared the whole of the contents had undergone polymerization. Probably the rapidity with which the diene, still unchanged at the end of the heating period, had polymerized at room temperature was due to "seeding" by the polymer already formed. The contents of the tubes consisted of two clearly distinct parts, namely, a clear, elastic lower portion representing the result of heat polymerization and an upper portion which almost filled the rest of the tube and consisted of the typical white "cauliflower" masses characteristic of cold-polymerized dimethylbutadiene. The heat polymer was about 28% of the whole. The tubes were allowed to stand for three and a half years in all; they were then opened, the two portions were separated and were then employed in the following experiments with as little delay as possible, being kept in an atmosphere of carbon dioxide in the meantime.

Since both the "heat" and the "cold" polymers appeared to be susceptible to oxidation (a few days' exposure to the air caused them to become sticky) an

antioxidant was added to all compounded stocks. Anhydro-aldol-α-naphthylamine proved to be effective in this connection. It prevented oxidation of methyl rubber in compounds kept uncured for at least six weeks.

On the mill the behavior of the cold polymer was noticeably different from that of natural rubber. It was at first crumbly and fell through the rolls, but by continued treatment on hot rolls it became more plastic, and eventually

TABLE I

PHYSICAL PROPERTIES OF NATURAL AND METHYL RUBBER AT 20° C. IN GUM AND CARBON BLACK STOCKS

Cure	Gum stock*						Cure	Gum stock+25 pt. carbon black +1.5 pt. stearic acid				
	T_2	T_5	T_6	T_B	E_B	Set		T_2	T_5	T_B	E_B	Set
I. *Smoked sheet*												
5′/110° C.	—	—	—	3	—	—	15′/110° C.	9.2	85.6	155	606	12.3
10	6.2	19.9	33.7	168	875	10.5	20	13.1	133.5	251	636	18.9
15	10.7	41.2	85.3	274	834	16.4	25	17.5	196	273	580	25.8
20	12.2	62.8	134.0	282	754	22.5	30	19.7	194	349	650	30.3
25	15.1	82.8	172	277	709	24.7	30	19.3	193.5	346	648	39.0
30	16.1	96.8	194	293	710	25.4						
20′/133° C.				24	206							
40				16.4	164							
60				15.5	161							
II. *Methyl rubber* (heat polymer)												
20′/110° C.		10.9		16.8	788	2.2	40′/110° C.		93.2	150.7	611	10.0
30		17.1		21.5	610	1.0	60		150.0	166.5	531	12.3
40		26.2		28.2	509	1.0						
20′/133° C.		—		28.2	365	1.1						
III. *Methyl rubber* (cold polymer)												
30′/110° C.	26.6			77.6	293	2.7	20′/133° C.	55.4		155	340	9.2
20′/133° C.	25.0			86.4	243	1.1	20	54.2		161	302	10.0
40	25.4			68.4	228	1.1	40	90.0		153	278	10.5
60	24.6			81.0	241	1.0	Gum stock+50 carbon black+1.5 stearic acid					
80	22.0			76.1	245	1.2						
							20′/133° C.	101		129	258	12.6
							40	133		156	259	22.4
							60	123		130	217	19.1
							(+ 5% plasticizer) 20′	87		153	350	16.9
							(+10% plasticizer) 20′	65		122	355	15.7
IV. *Methyl rubber* (heat and cold polymers, 50:50)												
30′/110° C.		17.5		33.3	610	2.7						
40		31.0		42.0	535	2.7						
20′/133° C.		—		51.0	400	2.2						

**Gum stock:– 100 pt. rubber, 3 pt. sulphur, 5 pt. zinc oxide, 1 pt. anhydro-aldol-α-naphthylamine, 1 pt. piperidinium pentamethylene dithiocarbamate.*

Tensile strength given in kg. per sq. cm.; elongations and set in per cent. T_2, T_5 T_6 = tensile strength at 200, 500 and 600% elongation respectively. T_B = tensile strength at break; E_B = per cent elongation at break.

there was obtained a sheet, which however was leathery and devoid of tack. The cold polymer took about twice as long to mill as natural rubber. The heat polymer broke down on the mill quite readily and in a similar manner to natural rubber, but a sheet of compounded stock from the heat polymer was noticeably less tacky than a corresponding sheet from natural rubber.

Vulcanization was carried out in moulds designed to produce moulded ring test pieces. These moulds, which were designed by D. F. Stedman, and will shortly be described by him in this Journal, do not involve any waste of rubber in producing test pieces and are well adapted for working with small quantities of material. Strips about 14 cm. long and weighing about 1.5 gm. were cut from the milled sheets and placed in the ring moulds. The latter were then placed in a small hydraulic press and a pressure of 1000-4000 lb. per sq. in. applied for 10-15 min. in order to make the strips fit the moulds perfectly. Vulcanization was then brought about by heating the moulds in a constant-temperature bath at either 110° or 133° C. for various periods of time. The moulded test rings thus secured were of standard diameter (44.5 mm.) and thickness (3.15 mm.) and of a height which varied slightly according to the amount of rubber used but was approximately 2.5 mm. The tensile strength and elongation of the test pieces were determined 24 hr. after curing by means of a Schopper machine which gave an autographic load-strain curve. Set was determined by measuring the length of the test pieces 30 min. after rupture. The set as thus determined is substantially all permanent set, as measurements of test pieces several days after rupture did not indicate any further retraction and as heating to 68° C. for five minutes also failed to produce further retraction.

The results are given in Table I, the figures given for the stocks containing natural rubber represent the mean of the results for three test pieces in each case; those for the methyl rubber stocks in most, but, owing to the limited amount of material, not all cases represent the mean of the results for two test pieces.

The plasticizer used in certain stocks as noted in the table was methylcyclohexyl adipate.

Retraction of methyl rubber. The results given in Table II show the rate of retraction at room temperature (20° C.) and at 45° C. when samples 5 cm. long of various vulcanized stocks from methyl rubber are stretched 150% for three minutes and then allowed to retract under no-load. For comparison, a properly cured and an undercured sample (see Table I) of natural rubber are included. It will be observed that the slow rate of retraction at 20° C. of the methyl rubbers in a gum stock is similar to that of the badly undercured sample of natural rubber.

Effect of temperature on the physical properties of methyl rubber. It has already been pointed out that, although vulcanized methyl rubber, especially if prepared from the cold polymer, is sluggish at room temperature, it becomes readily retractible at elevated temperatures, and at 70° C. or more has a "snap" similar to that of vulcanized natural rubber. Furthermore, if vulcanized methyl rubber is stretched at temperatures below its elasticity temperature,

TABLE II

RATE OF RETRACTION OF VULCANIZED NATURAL AND METHYL RUBBER
(GUM STOCK AS GIVEN IN TABLE I)
SPECIMENS EXTENDED 150% FOR THREE MINUTES AND ALLOWED TO RETRACT

Sample	Cure	Set after:				
		0.25 min.	0.75 min.	2 min.	4 min.	30 min.
At 20° C.						
Natural rubber	5′/110° C.	8.0	5.6	3.0	2.2	2.0
Natural rubber	20′/110° C.	2.0	1.2	1.0	1.0	1.0
Heat polymer	30′/110° C.	10.0	4.0	1.0	1.2	0.4
Cold polymer	40′/133° C.	9.0	6.0	1.0	1.0	1.0
Cold polymer+25 pt. C. black	40′/133° C.	22.2	13.0	7.0	5.0	2.4
Cold polymer+50 pt. C. black	20′/133° C.	56.0	29.0	15.0	9.9	4.8
Same+10 pt. plasticizer	20′/133° C.	30.0	16.0	9.0	7.2	3.4
Unvulcanized heat polymer		50.0	35.0	24.0	16.0	10.0
At 45° C.						
Heat polymer	30′/110° C.	10.0	2.4	1.6	1.6	1.6
Cold polymer	30′/110° C.	6.0	2.0	1.0	1.0	1.0
Cold polymer+25 pt. C. black	40′/133° C.	3.6	2.2	1.2	0.4	0.4
Cold polymer+50 pt. C. black	20′/133° C.	8.0	5.6	3.6	2.6	2.6
Same+10 pt. plasticizer	20′/133° C.	9.0	4.4	2.8	1.6	1.2

say 1° C., it will remain stretched and will not retract until warmed. Its behavior in this respect is similar to that of raw rubber. In order to study more closely the effect of temperature on methyl rubber, in comparison with its effect on natural rubber, a series of tensile measurements were made at temperatures of 5°, 20°, 37° and 70° C.

For the purpose of these measurements there was made and mounted on a Schopper testing machine a constant-temperature bath which permitted the specimens to be immersed in water at the desired temperature along its entire length up to the point of rupture. The bath consisted of a long rectangular metal tank, 34 by 3.5 by 4 in., with a hole in the bottom to allow the passage of the rod carrying the lower grip. By means of a packing gland of oil and graphite, the hole was made water-tight. Electrically regulated immersion heaters were inserted in the tank, and the water was stirred by means of a stream of air, which proved more satisfactory than a mechanical stirrer. Repeated tests with ordinary rubber showed that the effect of immersion in water during the short period of the test was negligible. The specimens were immersed without tension for a short time in the water before stretching, in order to allow them to come to temperature. Grips for holding the ring shaped test pieces presented a little difficulty at first, because it was found

TABLE III

THE EFFECT OF TEMPERATURE ON THE STRESS-STRAIN PROPERTIES OF NATURAL AND METHYL RUBBER

	Heat polymer	Cold polymer	Heat and cold polymers (50:50)	Heat polymer+25 pt. carbon black	Cold polymer+25 pt. carbon black	Smoked sheet	Smoked sheet+25 pt. carbon black
Temperature, 5° C.							
Cure	40′/110° C.	60′/110° C.	20′/133° C.		40′/133° C.	20′/110° C.	30′/110° C.
T_3	33.1	36.0	86.6			22.3	72.2
T_5						131	264
T_B	181	64	161		138	272	350
E_B	516	393	411		230	622	593
Set	4.5	6.1	4.7			20.2	35.0
Temperature, 20° C.							
Cure	40′/110° C.	30′/110° C. 40′/133° C.	40′/110° C. 20′/133° C.	40′/110° C. 60′/110° C.	40′/133° C.	20′/110° C.	30′/110° C.
T_3	19.2	25.4	7.8 18.5	32.0 49.0		18.6	48.0
T_5	26.2		31.0			80.8	194
T_B	28.2	77.6 68.4	42.0 51.0	150.7 166.5	153	285	347
E_B	509	293 228	535 400	611 531	278	694	649
Set	1.0	2.7 1.1	2.2 2.2	10.0 12.3	10.5	18.6	34.4
Temperature, 37° C.							
Cure	40′/110° C.	60′/110° C. 40′/133° C.	40′/110° C.		40′/110° C.	20′/110° C.	30′/110° C.
T_3	8.1	6.8 5.0	6.1			17.1	38.7
T_5						48.5	140
T_B	14.8	13.2 10.9	22.3		55.0	219	285
E_B	360	317 280	475		230	712	668
Set	0.9		3.4		5.6	19.5	43.5
Temperature, 70° C.							
Cure	40′/110° C.	40′/133° C.	20′/133° C.	40′/110° C. 60′/110° C.	40′/110° C.	20′/110° C.	30′/110° C.
T_3				15.3 25.4	25.9	15.1	28.8
T_5						36.1	84.9
T_B	6.2	2.4	5.4	23.1 26.3	26.3	106.5	185.5
E_B	230	180	191	380 306	306	680	685
Set	1.1	1.0	1.1		4.5	21.4	

NOTE:— *Stock: 100 pt. rubber or methyl rubber, 3 pt. sulphur, 5 pt. zinc oxide, 1 pt. anhydro-aldol-α-naphthylamine, 1 pt. piperidinium pentamethylene dithiocarbamate.*

that rotation of the test piece was essential for proper results. The required rotation was secured by using at each end of the testing machine gap two ball-bearing pulleys spaced horizontally. The pulleys, which were grooved, were about 1.4 cm. in diameter and about 3 cm. between centres. Using this arrangement, it was found that the test piece rotated as tension was applied, and there was no indication of the rubber being cut at the point of contact. Substantially similar results were obtained in comparative tests using these pulleys in the bath, and then substituting the standard mechanically rotated pulleys of the Schopper machine and carrying out tests at the same temperature in the air.

Selected cures of the same series of stocks (a gum stock and a carbon black stock) as had already been tested at room temperature (Table I) were put through tests at the other temperatures mentioned. The results are given in Table III.

Behavior towards swelling agents. In benzene and in chloroform the cold polymer only partly dissolved after seven days and left a large swollen residue; the heat polymer was nearly all dissolved after two days, although even after seven days there still remained a small undispersed residue. After seven days in ether, the cold polymer was slightly swollen but undissolved; the heat polymer had dissolved to the extent of nearly one-half. The cold polymer swelled in ethyl benzoate and in piperidine, but only a small portion had dissolved after seven days. Nearly one-half of the heat polymer dissolved in these liquids in two days, but it had not all dispersed after seven days. The above observations indicate the mean molecular weight of the cold polymer is markedly higher than that of the heat polymer, and that both materials are composed of a mixture of molecules in different states of polymerization (cf. 11).

The swelling of samples of the methyl rubber and of natural rubber cured under similar conditions in the gum stock was measured with the results given in the following table.

TABLE IV

SWELLING OF VULCANIZED METHYL RUBBER, SYNTHETIC ISOPRENE RUBBER AND NATURAL RUBBER

SAMPLES CURED FOR 30 MIN. AT 110° C. IN THE GUM STOCK QUOTED IN TABLE I

	Gm. liquid imbibed by 0.1 gm.							
	Cold polymer		Heat polymer		Natural rubber		Synthetic isoprene rubber*	
	1 day	2 days	1 day	2 days	1 day	2 days	1 day	2 days
Benzene	0.330	0.3305	0.370	0.371	0.345	0.345	0.330	0.330
Petrolic ether	0.190	0.190	0.210	0.211	0.180	0.180	0.1735	0.175

**In this case isoprene polymer obtained by polymerization in emulsion was vulcanized for 40 min. at 110° C.*

Vulcanization coefficient. Determinations of combined sulphur in comparable cured stocks gave the following results.

TABLE V

COMBINED SULPHUR IN VULCANIZED METHYL AND NATURAL RUBBER

	Combined sulphur as percentage of rubber	
	Cure, 30 min./110° C.	Cure, 20 min./133° C.
Natural rubber	3.09	3.11
Heat polymer	2.42	3.01
Cold polymer	1.89	3.05

Stock: Rubber, 100; S, 3; ZnO, 3; anhydro-aldol-α-naphthylamine, 1; piperidinium pentamethylene-dithiocarbamate, 1.

The total sulphur in the stock was 3.27% (expressed on the rubber). Of this the accelerator contributes 0.27%. Judging from the results for the natural rubber samples it would seem that about 0.17% of sulphur from the accelerators remains extractable.

Acknowledgment

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THE PREPARATION OF β-ARYLETHYLAMINES FROM α-CYANO-β-ARYLACRYLIC ACIDS[1]

By John Alexander McRae[2] and William Henry Vining[3]

Abstract

Details are given of a method by which β-arylethylamines can be prepared from α-cyano-β-arylacrylic acids. Conditions for the elimination of carbon dioxide from several α-cyano-β-phenylacrylic acids have been studied and, in agreement with the results of others, copper powder proved to be the most useful catalyst among the substances tried. The action of alkaline hypobromite solutions on phenyl- and piperonyl-succinimides resulted only in hydrolysis to the respective succinic acids.

It was shown several years ago by Baker and Lapworth (1) that α-cyano-β-arylacrylic acids can be reduced readily to α-cyano-β-arylpropionic acids and it has been shown further by Baker and Robinson (2) that α-cyano-β-piperonylpropionic acid thus prepared can be converted smoothly into β-piperonylpropionic nitrile. They state further that this nitrile is changed easily into the corresponding amide by Radziszewski's method. Prior to the publication of these papers we had carried out somewhat similar experiments, of which an account is now given, starting with several α-cyano-β-arylacrylic acids with the object of testing the feasibility of using the following scheme for the preparation of β-arylethylamines;

$$R.CHO \longrightarrow RCH{:}C(CN)CO_2H \longrightarrow RCH_2.CH(CN)CO_2H \longrightarrow RCH_2.CH_2CN \longrightarrow R.CH_2.CH_2.CONH_2 \longrightarrow RCH_2.CH_2NH_2.$$

To the authors this seems to have certain advantages over the following scheme, which is usually used (Slotta and Heller (9) have summarized recently the applications of this and other methods for preparing β-arylethylamines),

$$RCHO \longrightarrow RCH{:}CHCO_2H \text{ or } RCH{:}CH(CO_2Et) \longrightarrow RCH_2.CH_2CO_2H \longrightarrow RCH_2.CH_2.COCl \longrightarrow RCH_2CH_2CONH_2 \longrightarrow RCH_2CH_2NH_2,$$

in that the amides required for the last step are produced directly from α-cyano-β-arylacrylic acids, and these acids Lapworth and McRae (6), and Baker and Lapworth (1) have shown, are readily accessible substances.

The α-cyano-β-arylacrylic acids employed were those derived from benzaldehyde, anisaldehyde, piperonal, vanillin and veratric aldehyde. In each case excellent yields of the reduced acids were obtained by using as the reducing agent sodium amalgam prepared according to the directions of Raiford and Clark (8). The elimination of carbon dioxide from the α-cyano-β-arylpropionic acids, $RCH_2.CH(CN)CO_2H$, takes place easily by heating the acids with copper powder or preferably quinoline. Hydrolysis of the resulting nitriles,

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$RCH_2.CH_2CN$, was effected by means of cold, fuming hydrochloric acid, which we prefer to the Radziszewski method. As the result of numerous experiments the writers have been able to obtain uniformly high yields of β-arylethylamines from β-arylpropionamides through the action of alkaline sodium hypobromite which, contrary to the experiences of others, gave in this work better yields than alkaline sodium hypochlorite.

The yields in the various stages based on many experiments are as follows:

TABLE I

AVERAGE YIELDS OBTAINED IN CONVERSION OF α-CYANO-β-ARYLACRYLIC ACIDS INTO β-PHENYLETHYLAMINES

α-Cyano-β-aryl-acrylic acid from	I. Reduction (sodium amalgam), %	II. Elimination of CO_2 (quinoline as catalyst), %	III. Hydrolysis (fuming HCl)	IV. Conversion to amine, (NaBrO+ NaOH), %
1. Benzaldehyde	95	80–83	Almost quant.	66
2. Anisaldehyde	90–95	80–82	Almost quant.	80
3. Piperonal	95	80	Almost quant.	70
4. Vanillin	95	69	——	——
5. Veratric aldehyde	90	75	Almost quant.	70

The proposed method, therefore, gives good yields at all stages. An attempt to prepare histamine by applying this scheme to glyoxaline-(4 or 5)-formaldehyde failed. The authors were unable to bring about the initial condensation of this aldehyde with cyanoacetic acid.

Concurrently, a series of experiments on the elimination of carbon dioxide from α-cyano-β-arylacrylic acids using the acids from benzaldehyde and piperonal showed that of the various catalysts employed, copper powder was the most effective; quinoline with acids of this type promoted resinification to such a marked degree that it was useless for the purpose in mind.

A number of attempts were made to prepare β-aryl-β-carboxylic-ethylamines or, alternatively, β-aryl-β-aminopropionic acids by the action of alkaline sodium hypobromite on aryl-succinimides, using phenyl- and *piperonyl*- succinimides as examples, but hydrolysis to the corresponding acid was the only change observed.

Experimental

A. Reduction of α-Cyano-β-arylacrylic Acids

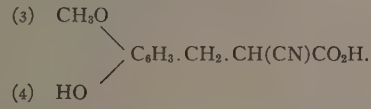
The α-cyano-β-arylacrylic acids used were prepared by the general method of Lapworth and McRae (6). The crude acids so obtained from the condensation of the aromatic aldehydes with sodium cyanoacetate were washed with benzene and recrystallized from dilute ethyl alcohol.

α-Cyano-β-veratrylacrylic acid was made also by the methylation of α-cyano-β-(3-methoxy-4-hydroxyphenyl) acrylic acid in alkaline solution by means of dimethyl sulphate but the method is less advantageous than that of first methylating vanillin to veratric aldehyde and condensing the latter with sodium cyanoacetate.

As reducing agents (a) sodium amalgam, (b) electrolytic reduction with a mercury cathode, (c) hydrogen in presence of colloidal palladium, and (d) aluminium-mercury couple on the ammonium salt of the acid, were tried. By far the most satisfactory and convenient reducing agent is sodium amalgam, made according to the directions of Raiford and Clark (8). Using amalgam prepared thus, the reduced acids obtained on acidifying the reaction mixture solidified rapidly, whereas with sodium amalgam prepared in the ordinary way crystallization was frequently delayed greatly. In most of these experiments the α-cyano-β-arylacrylic acids were dissolved in N/1NaOH, an equivalent of sodium bicarbonate was added and the reduction carried out at 35° C., using a 25-50% excess of sodium amalgam. This procedure presents no advantage over that used by Baker and Lapworth.

Although from time to time comparatively large amounts of cyanophenylacrylic acid have been reduced in this laboratory, at no time have the writers observed the interesting by-product isolated by Baker and Lapworth in one of their experiments. The α-cyano-β-arylpropionic acids were purified and agreed with the descriptions given by previous authors. The following acid, however, had not been prepared hitherto.

α-Cyano-β-(3-methoxy-4-hydroxyphenyl)-propionic Acid (α-Cyano-β-vanillylpropionic acid)



α-Cyano-β-vanillylacrylic acid (43 gm.) was suspended in 200 cc. of water. Five hundred grams of 2½% sodium amalgam was added in five portions. Reduction takes place very readily and is marked by the disappearance of the yellow color of the sodium salt of the unreduced acid. On acidification only a small amount of oil separated. The solution was extracted thoroughly with ether and after removal of the ether the residual oil crystallized after standing 24 hr. The yield was 41 gm. After several recrystallizations from toluene, in which it is difficultly soluble, the acid had m.p. 80° C. The acid may be recrystallized conveniently on a large scale from hot water, although with this solvent it tends to form supersaturated solutions. The acid is very soluble in alcohol and ether but dissolves with difficulty in benzene and is almost insoluble in ligroin. Analysis: Calcd. for $C_{11}H_{11}O_4N$: C, 59.73; H, 4.98; N, 6.33%. Found: C, 59.51; H, 4.90; N, 6.55%.

B. Conversion of α-Cyano-β-arylpropionic Acids into β-Arylpropionic Nitriles

The five α-cyano-β-arylpropionic acids investigated readily lose carbon dioxide when heated above their melting points but the loss of carbon dioxide is accompanied at times by the formation of considerable tarry material. A number of comparative experiments showed that while copper powder greatly facilitates the removal of carbon dioxide, producing good yields of the

desired nitriles, yet quinoline brings about the same decomposition still more readily and better yields of the nitriles were obtained. The quinoline used was recovered easily.

1. *Hydrocinnamic nitrile*

This nitrile was obtained by heating 43.2 gm. of α-cyano-β-phenylpropionic acid with 14 cc. of quinoline at 145-150° C. until the evolution of carbon dioxide ceased. After shaking the crude nitrile with dilute hydrochloric acid to remove the quinoline, it was extracted with ether and dried over calcium chloride. After removal of the ether 27.2 gm. of hydrocinnamic nitrile boiling at 138-140° C./15 mm. was obtained.

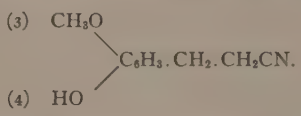
2. *β-Piperonylpropionic nitrile*

This was obtained by heating α-cyano-β-piperonylpropionic acid (73 gm.) with 16 cc. of quinoline at 170° C. until the evolution of carbon dioxide ceased. The crude nitrile was treated as described above and the pure nitrile obtained as a colorless oil distilling at 174-176° C./15 mm. Baker and Robinson (2) give the boiling point as 186-187° C./20 mm. The yield obtained was 81% of the calculated.

3. *β-Anisylpropionic nitrile*

α-Cyano-β-anisylpropionic acid (47 gm.) was heated with 10 cc. of quinoline in an oil bath at 160° C. until the evolution of carbon dioxide ceased. The nitrile was extracted as described above and after removal of the ether 32 gm. or 83% of the calculated quantity of the pure nitrile boiling at 172-173° C./23 mm. was obtained. Goldschmiedt and Fraenkel (4) obtained this nitrile by heating *p*-methoxyphenyl propionic acid with lead thiocyanate and gave the boiling point as 167° C./15 mm.

4. *β-Vanillylpropionic nitrile, β-(3-Methoxy-4-hydroxy) phenylpropionic nitrile*



Sixty grams of α-cyano-β-vanillylpropionic acid was heated with 17 cc. of quinoline at 160-170° C. in an oil bath until evolution of carbon dioxide ceased. After treatment as described above the nitrile was obtained as a colorless viscous oil distilling at 189-192° C./11 mm. The yield obtained was 36 gm. or 69% of the calculated. On standing the oil solidified and was recrystallized being obtained in prismatic needles from benzene and also from ether by precipitation with petroleum ether. M.p., 58° C. Analysis: Calcd. for $C_{10}H_{11}O_2N$: C, 67.8; H, 6.21; N, 7.91%. Found: C, 67.72; H, 6.25; N, 8.13%.

The substance produces a transitory sharp, stinging sensation when placed on the tongue. With ferric chloride a blue color is produced which fades rapidly to a dirty brown turbidity.

5. *β-Veratrylpropionic nitrile*

α-Cyano-β-veratrylpropionic acid (70.5 gm.) heated with 15 cc. of quinoline gave off carbon dioxide freely at 130° C. After evolution of the gas slackened the temperature was raised to 170° C. and maintained at that point until the decomposition was complete. The pure nitrile was obtained as before by fractionating under reduced pressure and agreed with the description given by Baker and Robinson. The average yield in five experiments was 75%.

C. Conversion of β-Arylpropionic Nitriles to β-Arylpropionic Amides

The method of Radziszewski (7) for the hydrolysis of nitriles was used successfully by Baker and Robinson (2) in the case of β-piperonylpropionic nitrile and this we have subsequently confirmed, but previously the authors' experience with alkaline hydrogen peroxide applied to phenylpropionic nitrile resulted in no hydrolysis, small yields of amide or complete conversion to the acid. The writers, therefore, discarded the use of that reagent in favor of fuming hydrochloric acid saturated at 0° C. and applied it to the foregoing nitriles. The procedure adopted was to treat the nitrile in a stoppered flask with 1½-2 times its weight of the fuming acid and allow the mixture to stand overnight in the ice chest. The amide which had separated was filtered without diluting on a sintered glass filter, the hydrochloric acid thoroughly removed and the amide recrystallized, if necessary, from the appropriate solvent. The phenyl-, piperonyl-, anisyl- and veratryl-propionamides so obtained had in each case the properties previously described. In general the crude amides were pure enough for immediate use in the Hofmann reaction. The average yields obtained in a series of each experiment with each nitrile were those stated above.

All attempts to prepare *β-vanillylpropionamide* from the corresponding nitrile either by the use of fuming, concentrated or dilute hydrochloric acid or caustic soda, gave either unchanged material or hydroferulic acid.

D. Preparation of β-Arylethylamines

Although alkaline sodium hypochlorite has been preferred by several authors to alkaline sodium hypobromite, our observations indicated that with the former reagent ammonia is more frequently evolved on heating the amide with the reagent than with the latter reagent and the yields of amine lower accordingly. The procedure finally adopted was uniform for each amide used and is illustrated sufficiently by the following preparation.

Preparation of β-Piperonylethylamine (Homopiperonylamine)

Sodium hydroxide (20 gm.) was dissolved in 150 cc. of water and the solution cooled to −10° C. Bromine (19.5 gm.) was dropped in slowly while the solution was stirred vigorously by mechanical means. Piperonyl propionamide (19.3 gm. = 1/10 mole) stirred into a paste with 24 cc. of water was added, using an additional 20 cc. of water for washing. After all the amide had dissolved 40 gm. of powdered sodium hydroxide was added and the solution

heated on the water bath at 85° C. for about 20 min. The amine which separated was extracted with ether, dried and distilled under reduced pressure. The homopiperonylamine had b.p. 145° C./11 mm. and was obtained in 70% yield.

Similarly, β-phenylethylamine, β-anisylethylamine and β-veratrylethylamine were obtained consistently in numerous experiments in 66, 80 and 70% yields respectively. Each of the amines was identified fully.

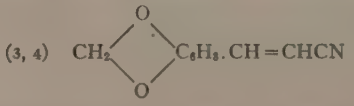
E. Elimination of Carbon Dioxide from α-Cyano-β-phenylacrylic Acids

Fiquet (3) and others have pointed out that arylidene-cyanoacetic acids lose carbon dioxide when heated above their melting points. Preliminary observations on the acid obtained by condensing benzaldehyde with sodium cyanoacetate and purified to a certain extent (a) by washing with benzene or (b) recrystallizing from alcohol, showed that the process of elimination of carbon dioxide was accompanied by considerable resinification. Accordingly the effect of the addition of various substances on this reaction has been studied. Quinoline and diethylaniline promoted resin formation to such a marked degree that any catalytic action on the elimination of carbon dioxide was completely masked. Aniline hydrochloride also promoted resinification. Heating the acid in presence of phosphoric acid and glycerol failed to effect any improvement in yields over those obtained by heating the acid alone. Copper powder on the other hand facilitated greatly the elimination of carbon dioxide and it was applied further for the preparation of β-piperonylacrylic- and β-anisylacrylic nitriles.

(1) *Cinnamic nitrile*

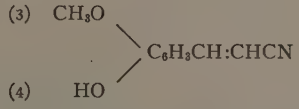
This was obtained by heating recrystallized α-cyano-β-phenylacrylic acid (17.3 gm.) with 34 gm. of copper powder in an oil bath at 180° C. for 30 min. The mixture was distilled in steam, the distillate extracted with ether and after removing the ether the residual oil was distilled under reduced pressure, 7.5 gm. being collected at 115-125° C./15 mm. Yield, 60%.

(2) *β-Piperonylacrylic Nitrile* (*3-4-methylenedioxy-cinnamic nitrile*)



α-Cyano-β-piperonylacrylic acid (21 gm.) was mixed with twice its weight of copper powder and heated at 185° C. for 30 min. The residue was extracted with ether and the crude nitrile, obtained by removal of the ether, was purified by either recrystallization from alcohol or distillation under reduced pressure, followed by recrystallization from hot alcohol from which it was deposited as a mass of minute colorless needles. M.p., 92° C., b.p., 163-170° C./14 mm. Analysis: Calcd. for $C_{10}H_7O_2N$: N, 8.1%. Found: N, 8.3%.

(3) *Vanillylacrylic Nitrile. 3-Methoxy-4-hydroxy-cinnamic Nitrile*

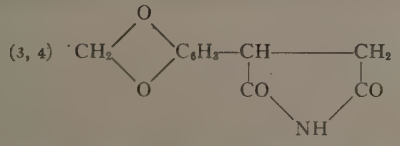


It was found that copper powder was of relatively small value in eliminating carbon dioxide from α-cyano-β-vanillylacrylic acid. Accordingly the cyano acid was heated rapidly in a Claisen flask under reduced pressure when a colorless liquid, distilling chiefly at 200-225° C./15 mm., passed over and solidified immediately. The crude substance was obtained in 60% yield and was recrystallized from dilute alcohol from which it was deposited in short truncated rectangular prisms. M.p. 112° C. Analysis: Calcd. for $C_{10}H_9O_2N$: N, 8.00%. Found: N, 8.39%. Ferric chloride added to an alcoholic solution of the substance produces an emerald green coloration, which changes on standing to a yellowish brown. A drop of an alcoholic solution of the substance placed on the tongue produces a sharp stinging sensation lasting but a few seconds. It dissolves in sodium hydroxide, forming a yellow solution, and in concentrated sulphuric acid, giving a deep red solution.

F. Action of Alkaline Sodium Hypobromite on Phenylsuccinimide and Piperonylsuccinimide

Although Hoogewerff and Van Dorp (5) obtained β-alanine in yields of 60% by the action of alkaline sodium hypobromite on succinimide, we failed to obtain even traces of any of the possible amino acids which might result from the application of this reagent to either phenylsuccinimide or piperonylsuccinimide. The exact procedure of these authors was used in several experiments. The imides dissolved readily in the alkaline hypobromite solution but, on heating, ammonia was evolved freely and only phenylsuccinic and piperonylsuccinic acids were isolated in good yield, although careful search was made for the expected amino acids. Less strongly alkaline solutions gave the same results. Prolonging the period in which the imide was left in the cold hypobromite solution before heating likewise effected no change. Further experiments on these reactions are in progress.

Piperonylsuccinimide (*3-4-methylenedioxyphenylsuccinimide*)



Piperonylsuccinic acid (6) was converted into its ammonium salt. The dry ammonium piperonylsuccinate was heated at 150-160° C. until evolution of ammonia ceased. The residue was dissolved in hot aqueous alcohol, which deposited crystals of piperonylsuccinimide on cooling. After several recrystallizations from alcohol the colorless crystals obtained had m.p. 169° C. Analysis: Calcd. for $C_{11}H_9O_4N$: C, 62.1; H, 4.11; N, 6.39%. Found: C, 61.7; H, 4.55; N, 6.57%.

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STUDIES ON HOMOGENEOUS FIRST ORDER GAS REACTIONS

II. THE DECOMPOSITION OF THE ISOMERIC ESTERS BUTYLIDENE DIACETATE AND ETHYLIDENE DIPROPIONATE[1]

By C. C. Coffin[2]

Abstract

The gaseous decompositions of the esters butylidene diacetate and ethylidene dipropionate have been studied from points of view previously outlined in papers on the decomposition of ethylidene diacetate (2, 3). The decomposition velocities have been measured at initial pressures of from 5 to 56 cm. of mercury and at temperatures between 211 and 265° C. The reactions are homogeneous and of the first order. They agree with the Arrhenius equation and give 100% yields (within experimental error) of an aldehyde and an anhydride. The preparation of the compounds and improvements in the technique of the velocity measurements are described.

While the specific velocities of the three reactions at any temperature are somewhat different, their activation energies are the same. It is suggested that in the case of such simple reactions, which are strictly localized within the molecular structure, the activation energy can be identified as the maximum energy that the reactive bonds may possess and still exist; *i.e.*, it may be taken as a measure of the stability of the bonds which are broken in the reaction. The suggestion is also made that for a series of reactions which have the same activation energy, the specific velocities can be taken as a relative measure of the number of internal degrees of freedom that contribute to the energy of activation. On the basis of these assumptions it becomes possible to use reaction-velocity measurements for the investigation of intramolecular energy exchange. The theoretical significance of the data is further discussed and the scope of future work in this connection is indicated.

The monomolecular velocity constants (sec^{-1}) of the decomposition of ethylidene diacetate, ethylidene dipropionate and butylidene diacetate are given respectively by the equations $\ln k = 23.74 - \frac{32,900}{RT}$, $\ln k = 23.96 - \frac{32,900}{RT}$, and $\ln k = 24.20 - \frac{32,900}{RT}$.

Introduction

During the last few years the kinetics of homogeneous first order gas reactions in general have been so satisfactorily elucidated that measurements of the velocity of simple monomolecular changes have acquired a distinct theoretical significance. The reaction must of course be "simple", *i.e.*, strictly localized within the molecule, before the activation energy can be identified with any particular mechanism or taken as a measure of the stability of the bond or bonds involved. The fact that the majority of the monomolecular reactions so far investigated are too complicated to furnish any detailed information regarding such questions does not detract from their value in clarifying the general mechanism of activation by collision, and in estimating the number of internal degrees of freedom that may contribute to the activation energy. A study of simple first order gas reactions is being carried out in this laboratory in an attempt to establish a connection between bond stability and activation energy, as well as to determine the relations between molecular structure and the number of internal degrees of freedom available for activation.

[1] *Manuscript received February 13, 1932.*
Contribution from the Department of Chemistry, Dalhousie University, Halifax, Canada.

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The mechanism by which esters of the general formula $R'CH\langle^{OOCR''}_{OOCR'''}$ decompose on heating has been indicated and the break up of ethylidene diacetate in particular has been discussed in previous communications (2, 3). The present paper deals with the decomposition of two isomeric homologues of ethylidene diacetate, *viz.*, ethylidene dipropionate and butylidene diacetate which, like ethylidene diacetate, break up homogeneously by the monomolecular mechanism to give quantitative yields of an aldehyde and an anhydride. This reaction, the mechanism of which appears to remain the same throughout the series of compounds, may thus be expected to lead to interesting data regarding the effect of molecular structure on the rate of chemical change. The simplicity of the reaction, which is essentially the change of an ether oxygen to a carbonyl oxygen, is an important factor in connection with the significance of the velocity measurements.

It has been found that while the specific velocities of these three ester decompositions are slightly different at any temperature, their energies of activation are the same within experimental error. Whether or not this energy (32,900 cal. per mole) is characteristic of the conversion of an ethereal to a carbonyl oxygen or of the breaking of two $-\overset{|}{\underset{|}{C}}-O-$ bonds is being investigated by studying other reactions where the same apparent structural shift occurs. Thus the low temperature gaseous decompositions of the paraldehydes and the acetals have been found to be homogeneous first order reactions, and are being studied with the view of determining the effect of intramolecular environment on the energy necessary to rupture the bonds in question.

With regard to the velocities of the ester decompositions, the working hypothesis is advanced that, since the activation energy is the same in each case, the reaction rate is directly proportional to the number of internal degrees of freedom involved in the activation. Whether or not it will be possible to determine in any instance the actual number of contributory degrees of freedom is not yet clear, as no falling-off of the velocity constant has been observed at pressures as low as 5 cm. of mercury. An attempt is being made to do this in the case of the simplest member of the series, *viz.*, formylidene diformate.

Experimental

Apparatus and Technique

The first 17 runs with butylidene diacetate and the first 3 runs with ethylidene dipropionate were carried out in the apparatus already described (3). All the remaining runs were made in a new and improved apparatus of the same general design. The volume of the new reaction tube was made much larger than the first (262.5 cc. as against 120 cc.) in order to obtain increased accuracy as well as sufficient amounts of reaction products for analysis. To avoid possible cooling of the reaction chamber by the reflux, the mercury was returned from the condenser to the boiler by a small-bore mercury-sealed tube outside the vapor jacket. To keep the reaction chamber from being splashed with super-

heated mercury, and to obtain a more uniform flow of mercury vapor through the jacket, the boiler was set about 20 cm. from the latter and was heated electrically. A thin-walled thermometer well ending just above the reaction chamber and below the wide-bore outlet to the condenser was let into the top of the vapor jacket. The temperature determined from the pressure on the boiling mercury was found to agree with that measured by a platinum resistance thermometer at this point within 0.1° C. The thermometer was a small platinum-in-quartz instrument having a resistance of 25.00 ω at 0° C. It was calibrated at the freezing and boiling points of water and the boiling point of sulphur. It may be mentioned incidentally that this thermometer well has been found to be very convenient for the calibration of thermometers and thermocouples for other work. As before, the vapor jacket and boiler were heavily lagged with asbestos and all connections were glass-sealed.

Other changes in the apparatus are as follows. The two-way stopcock T_1 (3, Fig. 1) was replaced by a three-way tap, of which one way led to a tube where the reaction products could be condensed with carbon dioxide and ether for analysis. The lower part of this tube, which could be evacuated independently of T_1, was connected to the upper part by a 2-cm. mercury-sealed ground-glass joint and so could be removed for weighing. For greater ease of control during a run a stopcock was inserted between the tubes E and N. To make the manometer readings independent of the barometric pressure the open side (see diagram) of M_2 was connected to the high vacuum side of M_3. The pressure in the vacuum sides of the two manometers was kept below 10^{-4} mm. by occasionally evacuating through the large-bore mercury-sealed stopcock T_6.

In the new apparatus the distance between the mark C and the ring seal connecting B with the vapor jacket was made as much as 10 cm. in order to eliminate the possibility of the mercury surface at C being at a temperature lower than that of its surroundings. As before, the readings of M_2 and M_3 agreed well within 1 mm. when B was evacuated and the mercury surfaces at C and M_1 were level. Correction must of course be made for the smaller density of the mercury in the hot side of the manometer $C-M_1$.

It should be pointed out here that a further series of low pressure runs with ethylidene diacetate has been made in an apparatus in which the manometer was kept at the temperature of boiling xylene (vap. press. Hg = 1.7 mm.) instead of at that of the reaction chamber. The velocity data, which will be dealt with in detail elsewhere, are in excellent agreement with those already published (3) and so afford definite evidence that mercury vapor at pressures between 1.7 and 100 mm. is without influence on the rate of these reactions.

Preparation and Purification of the Esters

The butylidene diacetate was prepared by refluxing equimolecular quantities of c.p. butyraldehyde and acetic anhydride in the presence of about 0.1% H_2SO_4. When equilibrium (b.p. 140° C. at 760 mm. (4)) was reached the catalyst was neutralized with a calculated excess of fused sodium acetate and the mixture was roughly fractionated *in vacuo*. The last fraction (butylidene diacetate

plus acetic anhydride) was washed several times with water and finally with dilute baryta to remove the anhydride, dried over $CaCl_2$ and fractionated twice at atmospheric pressure. The middle fifth of the last fractionation was taken for these experiments. It boiled at 212° C., melted sharply at −6.5° C. and analyzed 0.5% acetic acid.

The ethylidene dipropionate was prepared by circulating dry acetylene through water-free propionic acid at 100° C. in the presence of about 1% of mercuric sulphate (prepared *in situ* from HgO and excess oleum) as catalyst. When the acetylene absorption had ceased, the catalyst was neutralized with an excess of fused sodium propionate and fractionated *in vacuo*. The last fraction was washed free of propionic acid with dilute baryta, dried with $CaCl_2$, and fractionated several times at atmospheric pressure. The middle third from the last fractionation was twice recrystallized and used for the decomposition experiments. It boiled at 191°, melted at about −19° C. and analyzed 2.2 per cent propionic acid. The acid in this ester, which appears to be more difficult to purify than the other two, was taken into account in the velocity measurements. Only a small yield of ethylidene dipropionate is obtained by this preparation, the greater part of the reacting propionic acid being converted to vinyl propionate.

Products of the Reactions

If the break up of butylidene diacetate and ethylidene dipropionate were strictly analogous to that of ethylidene diacetate, the reaction products would be butyraldehyde plus acetic anhydride, and acetaldehyde plus propionic anhydride respectively. A separate research (4) on the rate of formation of butylidene diacetate and on the equilibrium concentrations of aldehyde, anhydride and ester in the liquid state showed that below 200° C. the ester breaks up reversibly to butyraldehyde and acetic anhydride. Moreover in all the gaseous decompositions of this ester the pressure calculated by the ideal gas law from the weight of ester taken was equal (within about 2%) to half the final pressure obtained by back-extrapolation as already described (3). That is, the pressure just doubled during a run so that it is very improbable that products other than the aldehyde and anhydride were formed. In the case of this ester also the final pressure was practically stationary so that the extrapolations are more certain than those of the ethylidene diacetate runs, in which a very slow but continual pressure increase was observed. As with ethylidene diacetate, the value of the initial pressure calculated from the weight of the ester taken gave less satisfactory constants than were obtained by assuming the initial pressure to be equal to one-half the final pressure.

The agreement between the calculated and the observed pressures of ethylidene dipropionate was never as good as for the other two esters, presumably on account of the fact that the secondary reaction was somewhat faster and the extrapolation more uncertain than in the case of either ethylidene diacetate or butylidene diacetate. The fact also that the ethylidene dipropionate was not as pure as the other esters may have had something to do with this discrepancy. There seems, however, to be no reason for doubting that this ester also is decomposed quantitatively to an aldehyde and an anhydride.

In spite of many attempts to condense and analyze the reaction products no really satisfactory analysis was obtained. The quantitative condensation of such high boiling liquids appeared to be the main difficulty as the anhydride found was always less than that calculated on the basis of 100% ester decomposition. The discrepancy between the two values, however, was never large enough to suggest a decomposition other than that postulated. Since the back-extrapolated final pressure of every run was practically twice the back-extrapolated initial pressure and very nearly twice the calculated initial pressure, a 100% ester decomposition at all temperatures and pressures is assumed. Thus, as in the case of ethylidene diacetate, no correction is needed in the ordinary monomolecular equation for the velocity of the reverse reaction.

Results

Calculation of Velocity Constants

It was shown in the first paper of this series (3) that the monomolecular velocity constants of these decompositions are given by the expression

$$k = \frac{1}{t} 2.303 \log \frac{P_c}{2P_o - P},$$

where P_o is the pressure at the beginning of the reaction and P is the pressure at time t. The graphical method of evaluating k was also explained.

Instead of obtaining graphically an average velocity constant for all the runs at any one temperature, as was done in the case of ethylidene diacetate, the data of each butylidene diacetate and ethylidene dipropionate run were plotted separately on the same large scale as before, the best straight line was drawn through the points and the velocity constant was determined from its slope. These constants for all the butylidene diacetate and ethylidene dipropionate runs are given in column 6 of Table I, which includes also the temperatures at which the runs were made (column 2) the weights of ester used (column 3) the initial pressures, *i.e.*, one-half of the back-extrapolated final pressures (column 4) and the ratios P_o/weight of ester (column 5). It is not deemed necessary to include here any graphs of $\log \frac{P_o}{2P_o - P}$ against time as the curves for ethylidene diacetate (2, Fig. 2) are typical of these other esters. Practically all the butylidene diacetate runs gave perfectly straight lines until the reaction was at least 90% complete. The ethylidene dipropionate results were not as good as those for ethylidene diacetate and butylidene diacetate presumably on account of the above-mentioned uncertainty in determining the initial pressure. The velocity constants are not considered to be seriously in error, however, as their drift did not become appreciable until the reaction was 60-80% complete.

That the reaction velocity is independent of the initial pressure may be seen by comparing the values given in columns 4 and 6 of Table I for a set of runs at the same temperature. Thus in the butylidene diacetate runs 1, 2, 3, 4, 18 and 19 the initial pressures varied from 12 to 45.2 cm. without causing any appreciable trend in the velocity constant. In the ethylidene dipropionate

runs 1, 2, 3, 4, 5, 16, 17 and 18 the pressure varied from 8.3 to 55.5 cm. with the same result. There can thus be no doubt that the reactions are monomolecular.

The ratios in column 5 are included to show that the percentage decomposition is independent of pressure and to give an idea of the limits of error involved. No formal computation of errors has been attempted on account of the unknown extent of the deviation of such systems from the ideal gas laws, and because of the unknown (within a few per cent) purity of the difficultly analyzed esters. The consistent nature of the results obtained, however, indicate that the errors arising from such sources are relatively unimportant.

Homogeneity of the Reactions

In Runs 18 to 21 with butylidene diacetate and 4 to 9 with ethylidene dipropionate, the glass surface in contact with the decomposing ester was increased by loosely packing the reaction chamber with glass wool. As is evident from Table I no change in velocity occurred so that the reaction undoubtedly takes place homogeneously throughout the gas. These esters are similar to ethylidene diacetate in that several runs are sufficient to coat the interior of the reaction tube with a brown uneven film-like deposit, the growth or removal of which is without influence on the reaction rate. This film is considered to be the result of a side reaction, probably the polymerization of vinyl esters (3).

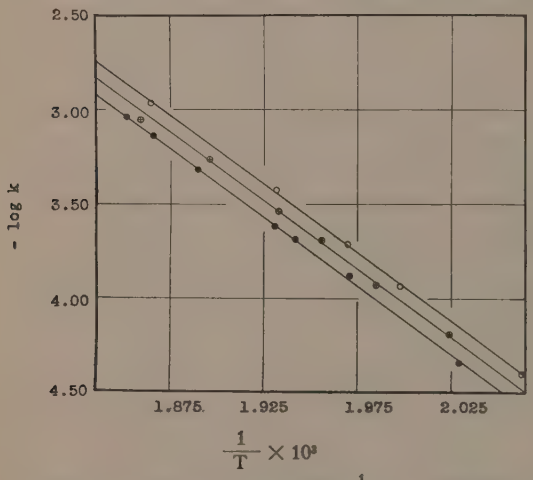

FIG. 1. *Graphs of -log k against* $\frac{1}{T}$. ●, *ethylidene diacetate;* ⊕, *ethylidene dipropionate;* ○, *butylidene diacetate.*

The Energy of Activation

In Table II is listed the reciprocal of the average absolute temperature (column 2) together with the negative logarithm of the average velocity constant (column 3) of all the ethylidene diacetate, butylidene diacetate and ethylidene dipropionate runs at each temperature. These values are plotted in Fig. 1 (ethylidene diacetate, ●; butylidene diacetate, ○; ethylidene dipropionate, ⊕), the straight lines of which were drawn parallel at a slope which would approximately fit all the points. This was done simply to emphasize, in the velocity-constant equations (column 4) and in the following discussion, the fact that the three activation energies are the same within experimental error, as well as to make the A's of the equation $\ln k = A - \frac{E}{RT}$ express the

observed differences of reaction rate. While such a procedure is admittedly arbitrary it is considered to be justified by the resulting simplification.

TABLE I

RESULTS OBTAINED IN RUNS WITH BUTYLIDENE DIACETATE AND ETHYLIDENE DIPROPIONATE

Run No.	$T°$, abs.	Weight of ester, gm.	P_0 cm. Hg.	Ratio $\frac{P_0}{\text{wt. of ester}}$	k (sec^{-1})
Butylidene diacetate					
1	517.8	0.2425	37.55	155	3.89×10^{-4}
2	517.9	0.1767	27.53	156	3.72×10^{-4}
3	517.8	0.1216	19.26	158	3.75×10^{-4}
4	517.7	0.2954	45.21	153	3.68×10^{-4}
5	535.9	0.1896	31.38	165	1.07×10^{-3}
6	536.0	0.1266	21.31	168	1.07×10^{-3}
7	536.1	0.0740	12.55	169	1.11×10^{-3}
8	552.0	0.1566	27.61	176	1.82×10^{-3}
9	507.6	0.2017	30.29	150	1.91×10^{-4}
10	507.6	0.2494	37.61	151	1.92×10^{-4}
11	507.6	0.1708	25.97	152	1.91×10^{-4}
12	507.6	0.0906	13.91	154	2.03×10^{-4}
13	484.4	0.1953	26.94	138	3.94×10^{-5}
14	485.5	0.3052	41.66	136	3.94×10^{-5}
15	484.6	0.1220	17.45	143	3.98×10^{-5}
16	500.4	0.1335	20.15	151	1.03×10^{-4}
17	500.4	0.1336	20.20	151	1.04×10^{-4}
18	517.8	0.1864	14.99	80.6	3.58×10^{-4}
19	517.8	0.1455	11.99	82.5	3.86×10^{-4}
20	500.5	0.1973	14.20	72.0	1.30×10^{-4}
21	500.6	0.1761	12.85	73.0	1.28×10^{-4}
Ethylidene dipropionate					
1	511.2	0.1348	19.95	148	2.02×10^{-4}
2	511.4	0.3121	44.40	142	2.19×10^{-4}
3	511.2	0.1749	25.56	146	2.11×10^{-4}
4	511.2	0.3690	26.23	71.2	1.95×10^{-4}
5	511.2	0.1170	8.28	70.8	1.97×10^{-4}
6	527.4	0.3746	27.79	74.3	5.44×10^{-4}
7	527.4	0.1393	10.08	72.3	5.50×10^{-4}
8	493.9	0.3581	24.04	67.1	6.2×10^{-5}
9	494.0	0.1399	9.50	67.9	7.0×10^{-5}
10	527.4	0.1690	12.25	72.1	5.57×10^{-4}
11	527.4	0.4150	31.75	76.5	5.35×10^{-4}
12	538.0	0.3966	29.02	73.3	9.10×10^{-4}
13	537.8	0.2091	15.40	73.8	8.70×10^{-4}
14	517.2	0.6483	45.46	70.1	2.72×10^{-4}
15	517.3	0.0867	6.25	72.1	3.10×10^{-4}
16	511.1	0.8019	55.49	69.1	1.87×10^{-4}
17	511.4	0.2218	15.47	69.9	2.19×10^{-4}
18	511.3	0.3346	23.28	69.6	1.98×10^{-4}
19	502.8	0.3933	26.87	68.5	1.15×10^{-4}
20	502.2	0.0904	6.30	69.6	1.24×10^{-4}
21	494.0	0.8245	53.0	64.4	6.40×10^{-5}

TABLE II

RECIPROCAL OF THE AVERAGE ABSOLUTE TEMPERATURE AND NEGATIVE LOGARITHM OF THE AVERAGE VELOCITY CONSTANT OF ALL RUNS WITH ETHYLIDENE DIACETATE, BUTYLIDENE DIACETATE AND ETHYLIDENE DIPROPIONATE AT EACH TEMPERATURE

Run No.	$\frac{1}{T} \times 10^3$	$-\log k$	$\ln k$
Ethylidene diacetate			
3, 4, 5, 6	1.942	3.688	
7, 8, 9	1.852	3.039	
10, 11	1.890	3.319	
12, 13, 14, 15	1.931	3.618	
16, 17, 18, 19, 20	1.866	3.140	
21, 22, 23	1.971	3.879	
24, 25	2.029	4.343	$\ln k = 23.74 - \frac{32{,}900}{RT}$
Butylidene diacetate			
1, 2, 3, 4, 18, 19	1.932	3.426	
5, 6, 7	1.865	2.967	
9, 10, 11, 12	1.970	3.712	
13, 14, 15	2.063	4.403	
16, 17, 20, 21	1.998	3.935	$\ln k = 23.96 - \frac{32{,}900}{RT}$
Ethylidene dipropionate			
1, 2, 3, 4, 5, 16, 17, 18	1.956	3.690	
6, 7, 10, 11	1.896	3.262	
8, 9, 21	2.024	4.185	
12, 13	1.859	3.051	
14, 15	1.933	3.536	
19, 20	1.990	3.925	$\ln k = 24.20 - \frac{32{,}900}{RT}$

Discussion

As is pointed out above, the majority of the monomolecular reactions hitherto investigated involve the more or less complete irreversible shattering of the whole molecule, so that it is not surprising that in general the activation energy decreases with increase of molecular complexity and instability. In the case of less drastic reactions that are strictly confined to a definite part of the molecule, as are these ester decompositions, it is to be expected that the energy of activation will be more independent of molecular structure, and that it might even appear as a constant characteristic of a series of compounds.

It is of course realized that conclusions drawn from the behavior of only three compounds of a homologous series must be regarded as purely tentative in their application to the series as a whole, and that future investigation may modify them considerably. The points which are raised by these experiments, however, are deemed to be sufficiently interesting to justify the present attempt to fit them in with what is already known about the break up of complicated molecules.

The assumptions made by Rice and Ramsperger (11) and by Kassel (5, 6), in the development of their theories II and III, seem to form the best foundation

for a discussion of the mechanism of these ester decompositions. Accordingly it is supposed that, as soon as the particular bond at which the molecule splits has accumulated an energy in excess of E, the energy of activation, reaction occurs; that a molecule is activated when the internal degrees of freedom which can contribute their energy to the reactive bond share in any distribution an energy in excess of E; and that the chance of the energy distribution resulting in reaction is proportional to the energy in excess of E possessed by the contributory degrees of freedom. In order to account for the Lindemann (9) time lag it must also be assumed that different energy distributions among these degrees of freedom succeed one another at a finite rate in the isolated molecule. Molecular activation is thus a result of collisional bimolecular processes governed by the ordinary Maxwellian distribution while "bond activation" is an affair of the isolated molecule being the result of an energy distribution over part of the molecular structure. As stated above "bond activation" and reaction are taken to be simultaneous events.

The fact that a structural alteration not affecting the particular part of the molecule involved in the reaction leaves the activation energy unchanged, favors the view that the latter is simply the minimum energy that the bond (or bonds) must acquire in order to react, as against the less definite but more rigorously derived identification of E as the difference between the average energy of the molecules which react and the average energy of all molecules*. It is hoped that the hypothesis outlined in the following paragraphs may be general enough to dispose of the essential differences between these two views of the physical meaning to be assigned to the energy term of the Arrhenius equation. It is advanced primarily in an attempt to explain the mechanism of simple structural changes taking place monomolecularly in complicated molecules.

The very common assumption, that a definite fraction only of the total number of internal degrees of freedom can contribute to the energy required at the weak point of a complicated molecule for decomposition to occur, appears to necessitate the further assumption that there are barriers within the molecule over which energy cannot easily pass (this has been suggested before (10)). That is, the molecule may be considered as being divided into sections between which, under conditions where the reaction velocity is measurable, there is no energy exchange and of which only the one containing the reactive bond can contribute to the energy of activation. That such ideas do not conflict with the experimental data on this point is evident when it is remembered that in practically all cases the number of degrees of freedom required to account for the observed reaction velocity is considerably less than the total number available. It is of course possible that the number found necessary to account for the reaction rate is a statistical quantity, sometimes including one particular degree of freedom and sometimes another. If this should be the case the accompanying speculations are meaningless. It is hoped that this point will be more definitely decided by experiments already referred to in which the

** For discussions of the meaning of the energy of activation see references 1, 5, 8, 10, 12 and 13.*

effect of various radicals, attached at different positions with respect to the breaking bonds, upon the velocity constant and activation energy is being investigated.

For the present it is assumed that as far as internal energy distribution is concerned the molecule is divided into different sections "insulated" from one another. A quantum oscillator having a frequency not commensurable with that of its neighbors would act as such an insulator (6). Energy could thus be furnished to the section containing the reactive bond only by direct collisions involving that part of the molecule, or by any collisions of sufficient violence to somehow break down the sectional insulation.

In a gas consisting of such sectionalized molecules, a Maxwellian energy distribution will exist among the molecular sections as well as among the molecules themselves. As it is the distribution among the reactive sections with which the Arrhenius equation is concerned, the energy of activation may be defined as *the difference between the average energy of the reactive sections which react and the average energy of all the reactive sections*. Such a definition would seem to combine the rigor of Tolman's derivation (12, 13) with the advantages inherent in the simpler view of the activation energy as a critical increment.

It is thus evident that the energy of the unreactive sections and, hence the total energy of the molecule, will have little or no effect upon the mechanism of activation or reaction. Indeed the nonreactive sections of the molecule might well have an even smaller influence on the velocity constant than if they were present as a separate inert gas which could activate and deactivate by ordinary collisions. The molecular diameter, velocity and mean free path, and hence the number and violence of the collisions, would of course depend upon the size and number of nonreactive sections in the molecule. It is well known, however, that the influence of such factors on reaction rate is overshadowed by the energy factor. A more important effect might well arise from a cushion or "bumper" action of the inert sections which would tend to diminish the number of effective collisions and would thus constitute at least part of the mechanism underlying the non-distribution of energy that must be assumed in order to account for the velocity of certain reactions (7).

In a series of first order reactions which have the same activation energy E, the relative decomposition velocities at any temperature will be proportional to the number of activated molecules, and also to the probability that the reactive bond will accumulate, from its particular section of the molecule, an energy in excess of E. Both the number of activated molecules and the probability that an activated molecule will react before the end of its mean free time are dependent upon the number (n) of degrees of freedom in what has been called above the reactive section. Thus if n is very small no appreciable fraction of the molecules will have energy greater than E in their reactive sections until the temperature has attained a very high value. If, on the other hand, n is large the same amount of energy will be available for the reactive bond at a proportionately lower temperature. An increase of n will thus increase the number of activated molecules but will tend to diminish the proportion that react, for the reason that there will now be a greater number

of possible energy distributions within the reactive section, and the chance of the occurrence of the one necessary for reaction will be reduced. It is to be expected, however, that this latter effect will be very small for small increases in n and, for the present, may be considered negligible in comparison with the increase in velocity due to the greater number of activated molecules.

The above hypotheses offer at least a qualitative interpretation of the ester decompositions reported in this paper. The addition of two —CH_2— groups to ethylidene diacetate to form butylidene diacetate, and ethylidene dipropionate increases the reaction velocity without changing the energy of activation, and may thus be considered as simply adding to the number of degrees of freedom in the reactive section. That the magnitude of the velocity increase is dependent on the position of the added —CH_2— groups is evident from a comparison of the reaction rates and structures of the three compounds. Butylidene diacetate has the greatest and ethylidene diacetate the smallest velocity at any temperature, with ethylidene dipropionate about half-way between. In butylidene diacetate both —CH_2— groups are added to the aldehyde side of the ester while in ethylidene dipropionate both are on the anhydride side. The latter position would thus seem to be about half as effective as the former in adding to the degrees of freedom of the reactive section. Indeed, if the Arrhenius equation be written $\ln k = A - \frac{E}{RT}$ then, in a series of reactions having the same E, the numerical value of A may be taken as a relative measure of the number of degrees of freedom in the reactive section of the molecule. From Table II these values for ethylidene diacetate, ethylidene dipropionate and butylidene diacetate are respectively 23.74, 23.96 and 24.20. By studying the decompositions of other compounds of this series it is hoped to determine just what parts of the molecule can contribute energy to the reactive bonds and thus obtain information regarding the laws of intramolecular energy exchange. Further discussion of such matters will therefore be postponed until more experimental data are available.

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MEASUREMENT OF THE VISCOSITY OF GASES OVER A LARGE TEMPERATURE RANGE[1]

By B. P. Sutherland[2] and O. Maass[3]

Abstract

The work described is an investigation of the viscosity of air, hydrogen and carbon dioxide. The principle of damped oscillations was employed and an apparatus was built embodying many new features which make possible an accuracy greater than has hitherto been obtained. It was the attempt at the elimination of experimental error in the oscillating disk method which was the main feature of the investigation. At room temperatures where values in the literature are reliable excellent agreement with the best data has been obtained, but at lower temperatures where there is much divergence in published values the present results are of importance as giving more reliable and accurate data than hitherto available. For hydrogen and air the temperature range +20° to −200° C. was covered. In the case of carbon dioxide the range was limited by its properties to +20 to −95° C. As the temperature coefficient of the viscosity of gases is of particular interest from a theoretical point of view, as far as the kinetic theory is concerned, the data obtained may be considered important. Incidentally, Maxwell's law concerning the effect of pressure on viscosity was confirmed at the lowest temperature range hitherto investigated.

Introduction

The investigation of the viscosity of gases was really definitely begun by Graham about 84 years ago, and has been carried on by various workers with different types of apparatus up to the present. In spite of a vast amount of work and much data there is still a great deal of uncertainty and discordance, so that it becomes almost impossible to obtain sufficiently reliable data for satisfactory theoretical deductions. Even in the case of the viscosity of air at room temperature, upon which determination much labor has been expended, the value can be stated with certainty only to about 0.5%, and at lower temperatures there is so much divergence that it is impossible to deduce even a fairly good mean. The scarcity of reliable data at low temperatures is obvious from the survey of viscosity given in the International Critical Tables, where practically nothing is included on this property at low temperatures.

It was with a view to filling this gap to some extent and supplying data for theoretical deductions of molecular forces that the present work was undertaken. Unexpected difficulties and obstacles have hindered the covering of a wide field as yet, but it is believed that the results obtained are of a high order of accuracy and constitute a definite contribution to the subject. It is also expected that the increased knowledge of the best methods of attacking this problem will lead to further work on the viscosity of gases.

It would take too long to enumerate all the reasons for choosing the oscillating disk method for the determination of the viscosity of the gas. Suffice it

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to say that it was considered impossible to eliminate errors involved in the other methods when a large temperature range involving low temperatures was to be investigated, particularly when absolute values were to be determined.

The principle of damped oscillations was first used by O. E. Meyer (6, 7, 8). Tomlinson (12) and Hogg (2) further developed Meyer's method. Vogel (15) and Günther (1) evolved an apparatus which was the starting point of the one used by the present investigators.

Experimental Work

The marked improvements which have been made both in design of apparatus and experimental procedure will, it is hoped, be evident from the following description. The accompanying diagram (Fig. I) has been drawn fairly well to scale and will elucidate the description which follows.

The principle involved is the following. A circular disk is suspended in the gas so as to lie horizontally and is given a small torsional oscillation in its own plane. The rate at which the oscillations diminish is a measure of the viscosity of the surrounding gas.

Obviously a prime requisite is to have the place and means to hold the apparatus firmly and free from extraneous vibration. Such were obtained here in a room, partly below ground, in which the required supports were made by angle irons cemented into the wall. The apparatus itself was securely clamped to a heavy stand fitted with levelling screws. The stand was in turn clamped on to the wall bracket when accurately levelled. In this way it was found possible to keep the apparatus set in position as long as desired and unaffected by outside vibrations such as those due to work in other parts of the buildings.

The oscillating disk itself was made of silver, which is quite suitable for the purpose, and hung between two other disks of the same material, whereby the viscous drag was greatly increased. All three disks were 1 mm. thick. The swinging disk was 3 cm. in diameter and the fixed disks were about 4.5 cm. in diameter and were held apart by a spacing ring 3 mm. thick, the whole being fastened together with four small screws.

The amplitude of the oscillations was measured on a ground-glass scale by means of a beam of

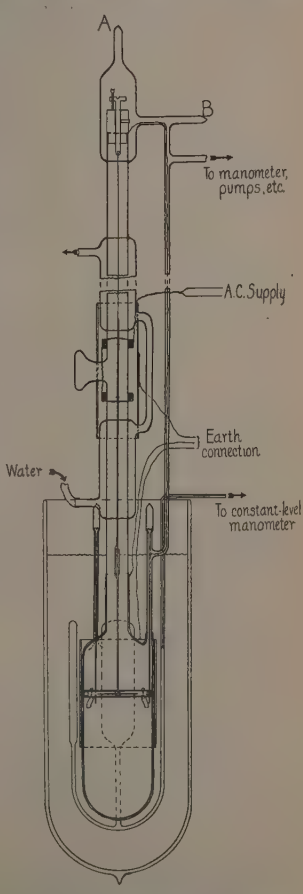

FIG. 1. *Apparatus for measuring the viscosity of gases over a large temperature range.*

light reflected from a small mirror mounted on a rod, which in turn was rigidly attached to the swinging disk. This rod was 1 mm. in diameter, about 25 cm. long, and a short section of it was made of ivory in order to hinder conduction of heat along it, as it was necessary to keep all of the upper part of the apparatus at constant temperature (25° C.) even though the lower part might be very cold.

The suspension wire carrying the rod and oscillating disks was of constantan, 0.001 inch in diameter and about 25 cm. long, and was attached to a hook fitting in an adjustable brass head so that it could be turned, raised or lowered and set in position. Though it was so fine, the wire was strong enough for the purpose and, with the particular dimensions here used, gave the system a period of oscillation of about 50 sec. Even after violent vibration due to accidents it was found to return to its original zero within very small limits.

The glass apparatus in which the whole was enclosed was of Pyrex and was made to order by The Fisher Scientific Company, its construction being clearly shown in the diagram. The jackets were for the circulation of water at 25° C. from a thermostat, to keep the suspension wire at constant temperature. Previously the water jackets had been of a removable type but the all-glass arrangement was an improvement. The construction at the head was so made that by blowing out the ends of the tubes *A* and *B* adjustments of the height or angular position of the disk could be made by means of a long screw-driver. Afterwards they could be sealed off again making the system air-tight.

Another respect in which this apparatus differed from previous ones was in the method of supporting the fixed disk. These were formerly fastened in place against the glass wall by means of litharge-glycerine cement. This was found to be unsatisfactory in that slight excess glycerine had an appreciable vapor pressure, and the cement itself was porous and very liable to absorb gases and then later give them out. In the present apparatus the disks were held in place with three rods whose heads rested in glass tubes as shown. These rods were threaded on the lower portions and fitted into holes in the edge of the disks. Accurate levelling could be done by merely turning the appropriate rods, their heads being slotted for the purpose. When the necessary adjustments had been made the ends of the tubes were sealed together ensuring the whole being air-tight.

Electrical connection was made between the disks by the wire shown which was entirely within a glass tube and connected with the head. The heat-insulating section of ivory was bridged by a very fine wire making electrical connection but having practically no heat effect.

Another feature of the glass work was the plane window opposite the mirror. This was formerly fixed on by means of sealing wax, but it was desired to avoid the use of all such materials if possible. Therefore it was fused on. An attempt was made to grind and polish the flattened end of a tube to form an optically true window but this was found very difficult to accomplish satisfactorily. Pyrex glass had to be used to make the join with the main apparatus. Finally some sheet Pyrex glass was supplied by the Corning Glass Works and it was found possible to fuse a disk of this to the end of a tube,

making a perfect join round the edges without heating the centre sufficiently to distort it. The over-all diameter of the piece made was about 3 cm. The central portion of this was entirely undistorted.

The original method of starting the oscillations was as follows: two small permanent magnets were astatically fixed to the rod of the oscillating disk and one of these was influenced with a permanent magnet from the outside. This was later replaced by a small solenoid through which a fixed current was passed when it was desired to produce a deflection and has again been substituted by two pairs of solenoids diametrically opposite one another. In this way a force is obtained on both magnets and this should closely approximate to a pure torque.

Further it was thought that the permanent magnets on the rod of the disk might themselves influence the results in two ways. First if they were not perfectly astatic there would be a tendency to set in one direction. Actually this was found to be the case and this direction was markedly affected by the presence of iron nearby. And secondly the force necessary to move the magnets through the earth's field would damp down the oscillations and so introduce an uncertain factor in the results. It is believed that these undesirable features have been almost entirely eliminated.

The two magnets themselves have been done away with and two small pieces of permalloy substituted. When starting the oscillations, the electrically produced field induces magnetism in these and by their tendency to align themselves with the field the oscillations are produced. On stopping the current the permalloy loses practically all its magnetism. Further the starting coils are all of the same size and connected in series, but the two pairs give opposite fields so that any residual magnetism should be neutralized. A source of supply of alternating current was obtained for starting, instead of direct current as heretofore, and this was gradually cut off each time so that the permalloy was demagnetized at the conclusion of each impulse. Care was taken to leave the coils on open circuit to avoid any induction effect due to the moving permalloy.

In order to prevent any effect from the earth's field or stray fields this section of the apparatus was encased in a shield of permalloy. As shown in the sketch, this extends considerably beyond the magnets and tests have shown it to be quite effective.

Electrostatic charges produced on the outside of the glass were found to produce violent motion of the disk inside, particularly when the apparatus was immersed in liquid air. This was overcome by the connection between the disks as mentioned above and by coating the outside of the glass with tin foil connected to ground. A permalloy shield around this section of the apparatus protected the moving disk from magnetic fields and was also grounded, as was the upper shield.

With these devices no appreciable effects from electrical or magnetic causes were observable under conditions which previously gave marked effects. Quite powerful permanent magnets are without any influence on the apparatus.

Accessory apparatus comprised the lamp and scale set. The lamp was of the type used in automobile headlights and gives a powerful concentrated beam. A new scale was made, 100 cm. long, and calibrated over the whole length. This was placed about nine feet from the mirror so the oscillations were magnified greatly. On such a long scale it is necessary to apply corrections for non-curvature. These have all been worked out and were used. This auxiliary apparatus was all firmly clamped on brackets similar to those on which the main apparatus was held.

From the viscosity apparatus a long zigzag tube, to avoid transmission of vibration, led to a McLeod gauge and mercury manometer. A Langmuir pump, Toepler pump, and containers of the various gases were connected when needed.

In setting up, the lower part of the apparatus was closed in an inverted position after the introduction of the disk. The small hook on the end of the suspension wire was inserted into the eye made for it in the brass head, and the apparatus was then set upright in its stand. The stand was then carefully levelled so that the swinging disk hung in the centre of the fixed disks. In this position it was rigidly clamped. Then the fixed disks were adjusted for horizontality by a cathetometer. Where these disks were supported with cement it was necessary to blow a small hole in the bottom of the apparatus so that adjustment might be made through this and the cement applied. This hole was afterwards sealed again. In the present form the adjustment was made by the long screws through the upper ends of the three tubes which were still open. Finally these tubes were sealed off.

The swinging disk was next adjusted so that it hung midway between the fixed disks and also so that the mirror threw the image approximately to the centre of the scale. When this was done the two tubes A and B were sealed off. It was necessary to have the scale perpendicular to the beam of light at the zero position. Adjustment of this was made from time to time as temperature and other effects produced slight shift of the zero.

A large Dewar flask of about $2\frac{1}{2}$ litres capacity served as the bath for regulating the temperature of the gas. For temperatures above 0° C. water was used for this, and then ether down to about $-100°$ C., cooling being done with solid carbon dioxide to about $-70°$ C., and then with liquid air. Low boiling naphtha enabled lower temperatures to be obtained, the lowest actually used with this being about $-123°$ C. Unfortunately this leaves rather a large gap before the next point which is that of liquid air (nearly all oxygen) about $-183°$ C. Liquid nitrogen (93%) gave about 10° C. lower and by bubbling a rapid stream of hydrogen gas through this the temperature was reduced further to a minimum of $-198.4°$ C. It is believed that under more favorable conditions of heat insulation this last method would be more effective and might be useful for conditions under which it was impossible to have the liquid under reduced pressure.

When needed, stirring of the bath was effected by a stream of dry air or hydrogen. Except in one or two cases the variation of temperature due to warming up during a run did not exceed 1° C., and at the higher temperatures

was much less than this. In all cases the variation was regular, so averaging gave accurate values.

Temperatures were measured by means of a hydrogen thermometer whose bulb was made in three parts as shown in the diagram. The reason for this shape was that it was desired to have a large volume distributed through the bath, and yet it had to be compact to fit into the Dewar vessel. The calibration was done by observations with a standard thermometer at room temperature and in liquid air, and showed that the ratio of volume of bulb to that of dead space was about 22. The temperature for the lower point was determined by ascertaining the proportion of oxygen in the gas coming off from the liquid air.

The corrections for variation in room temperature were calculated but were nearly always less than 0.1 mm. since the room temperature remained within a range of 2° C. most of the time. On the pressure scale, 0.2 mm. corresponds roughly to 0.1° C. of temperature, so temperature readings are correct to better than 0.2° C., the only uncertainty being when the temperature was changing relatively quickly.

The three gases used were carefully purified. Air was freed from moisture and carbon dioxide by passing through potassium hydroxide solution and sulphuric acid and then over phosphorus pentoxide.

Hydrogen was made in a Kipp generator from zinc and dilute sulphuric acid. The gas was passed through alkali hydroxide and sulphuric acid, dried over phosphorus pentoxide, and then passed through a bulb containing coconut charcoal at liquid air temperature.

Carbon dioxide was made from marble and dilute hydrochloric acid, and after purifying with carbonate solution and permanganate was dried and condensed to the solid by means of a carbon dioxide-ether mixture at reduced pressure. It was then slowly distilled over phosphorus pentoxide and condensed at $-78.5°$ C. under about $1\frac{1}{2}$ atm. It was stored under these conditions and before use was again passed over phosphorus pentoxide. A large portion was allowed to evaporate to ensure freedom from air or other non-condensable gases.

After some experience it was found advisable to have the apparatus at room temperature when a fresh gas was being introduced, in order as far as possible to prevent traces of the previous gas being held by adsorption. The apparatus was always pumped out, then filled with the new gas and allowed to stand for a while. It was then pumped out again and swept out several times before finally filling with the gas. The fact that samples of gas prepared at different times gave constant results is a proof not only of the reliability of the apparatus but also of the efficiency of the methods of purification.

The apparatus had first to be calibrated by using a gas whose viscosity was known. Air was chosen as being most suitable as its viscosity is fairly well determined at about 20° C., and in any case it is generally used as the standard of reference in other work. Accordingly the apparatus was pumped out and filled with air, free from carbon dioxide and carefully dried. After allowing time for it to come to the temperature of the bath the disk was set in oscillation and a number of consecutive readings were taken of the position of the image

on the scale at either end of its swings. Taking these in pairs and subtracting them obviously gives the amplitude of the oscillation, Ll, as read. A small correction for non-curvature is then applied giving the true amplitude, L. A sample set of readings is given in Table I to make this clearer. This was one of the standardization runs with air at 22.6° C.

TABLE I

STANDARDIZATION WITH AIR AT 22.6° C.

N	l	r	Ll	L	Log L	t
1	29.11	67.18	38.07	38.01	1.57990	0.00
2	31.12	65.23	34.11	34.06	1.53224	
3	32.94	63.52	30.58	30.54	1.48487	
4	34.52	61.97	27.45	27.42	1.43807	
5	36.00	60.60	24.60	24.58	1.39058	
6	37.31	59.37	22.06	22.04	1.34321	
7	38.49	58.22	19.73	19.71	1.29469	
8	39.51	57.25	17.74	17.73	1.24871	
9	40.46	56.35	15.89	15.88	1.20085	
10	41.32	55.58	14.26	14.25	1.15381	
11						831.0

In this table l and r are the readings to the left and right respectively. $Ll = r - l$, t is the time, taken by a stop watch, of a number of oscillations, in this case 10. This was measured from the time the image passed over the zero point of its swing in the direction left-to-right. The logarithmic decrement is now given by the difference between the values of log L for any two consecutive swings, and it is this function which gives at once a direct measure of the viscosity of the gas. Following Maxwell (4, 5) the set of readings as above was averaged by taking differences between the logarithms of the pairs: 1-10, 2-9, 3-8, 4-7, 5-6. If the logarithmic decrement is called λ then these differences will give respectively 9λ, 7λ, 5λ, 3λ, λ. These were now weighted by multiplying by their factors 9, 7, 5, 3 and 1 respectively, so that values of 81λ, 49λ, 25λ, 9λ and λ were obtained. These were added and divided by the total (165) giving the mean value of λ. The results obtained are shown in Table II.

TABLE II

$9\lambda = 0.42609$	$81\lambda = 3.83481$
$7\lambda = 0.33139$	$49\lambda = 2.31973$
$5\lambda = 0.23616$	$25\lambda = 1.18080$
$3\lambda = 0.14338$	$9\lambda = 0.43014$
$\lambda = 0.04737$	$\lambda = 0.04737$
	$165\lambda = 7.81285$
	whence $\lambda = 0.047351$

Two other such sets were obtained at the same time, the three being sufficiently close to allow of averaging.

In Table III, t is the time of one complete swing in seconds. The remarkably good agreement here shown is fairly conclusive proof that the apparatus is free from disturbing influences.

Before this value can be used for calculations it is necessary to determine certain corrections which have to be applied. In the first place the theory does

TABLE III

				Mean
λ	0.047351	0.047381	0.047387	0.047373
t, sec.	51.11	51.04	51.00	51.07
T, °C.	22.6	22.4	22.4	22.5

not give direct proportionality even for an ideal apparatus, but there is a variable factor which is expressed by Maxwell (4, 5) as a convergent series. The derivation of this would be out of place here but it may suffice to say that the first terms of the series were calculated for the case of air and are as follows, $1-0.00021+.00001-$etc. Obviously this can be put equal to 1 without affecting the accuracy of the results for present purposes.

The other corrections to be applied arise from the fact that other causes beside the drag of the gas on the disk will tend to damp down the oscillations. The rod attached to the disk and the mirror and magnets on it will all have a frictional force exerted on them by the gas, and as these parts are not at the temperature of the disk but at something close to 25° C. this force will not be constant in proportion to that on the disk. This force is supposed by Vogel (15) to be proportional to the square root of the viscosity but it is somewhat uncertain and not readily determined. In the present work the difficulty has been overcome by making these extra parts as small as possible so as to practically eliminate the effect. The mirror is about 2 by 3 mm. and the two magnets each about 2.5 by 0.8 mm. When it is remembered that the disk is 3 cm. in diameter, and the drag is proportional to the fourth power of the diameter it will be seen that the sum total of these is negligible, and as they are swinging freely in a wide tube the effect is again proportionately less. Experimentally these corrections can be determined only if the relative viscosity of two gases or of one gas at widely different temperatures is known. This method is used as a check and confirms the above conclusions.

It has already been explained how the possibility of magnetic and electrical effects causing a drag has been eliminated. Such little as may be left does not seem to be affected by any outside influences and so will be constant throughout.

Vibration will of course seriously affect the results. The substantial supports have reduced this to a minimum and if any unusual circumstances should cause such, it is readily noticeable. The period of oscillation in a transverse direction is so much smaller than that of torsional oscillation that such oscillation is visible in the movement of the image on the scale. Also it will make the results irregular so that if no such irregularity is found the apparatus may be presumed free from extraneous oscillations. In each case before beginning a set of readings the disk is brought to a practically steady position, then the swing of the desired magnitude is gradually built up. Before taking any readings a few complete swings are always allowed to take place to avoid any irregularities due to starting.

Thus there is left only one correction to be applied, namely, that for the internal friction of the wire suspension. This is of course independent of the gas being used and changes only with change in temperature of the wire. Such is avoided as far as possible by the jacket round all the upper part of the apparatus, which is thus kept close to 25° C. One difficulty arises here in that only a very slow stream of water can be passed through the jacket; otherwise a vibration is gradually built up. So, depending on the temperature of the lower part of the apparatus, the temperature of the incoming stream of water is varied to give a mean temperature of about 25° C. Thermometers in the water stream at the inlet and outlet show when this is obtained. If the elastic properties of the wire are affected by the temperature changes which do occur in it, the fact will be shown in changes in the period of oscillation. There is perhaps a slight decrease in the period when the lower part of the apparatus is very cold, but it is only a fraction of 1% and is not always observable, as the period is slightly lessened as the viscosity of the medium increases. Two cases in which the viscosity is about the same may be compared, namely, air at −185° and hydrogen at −100° C. The period was about 0.1% less in the former case.

The determination of the internal friction effect of the wire may be carried out directly by evacuating the system to a very low pressure, and observing the rate of decrease of the oscillations over a long period, such as one hour or more. The difficulty is to obtain the required high vacuum. As previously mentioned, a long connecting tube was used to avoid transmission of vibration and this greatly decreased the rate of diffusion of gas. Matters were improved by thoroughly sweeping out with hydrogen and then evacuating, but even so when the pump was running it was not at all certain that the pressure registered by the gauge was actually that in the apparatus. Indeed the following results prove that it was not.

After 15 hr. continuous pumping with a Langmuir pump backed by a Toepler pump the gauge showed a steady reading of 0.00003 mm. The mean of an extended series of readings gave a value of $\lambda = 0.001779$. After three days' pumping the gauge reading was still the same but $\lambda = 0.001460$, all being at room temperature. When the apparatus was cooled in liquid air the gauge reading fell to about 0.00002 mm., readings at these low pressures not being very certain, and the logarithmic decrement fell to 0.001234. The apparatus was then allowed to warm up again and after a further 12 hr. pumping the previous results at room temperature were closely repeated, namely $\lambda = 0.001466$ and $P = 0.00003$ mm. Unfortunately before further readings were taken, the Toepler pump broke down after nearly five days continuous running.

However, the pump was repaired and the apparatus once more filled with hydrogen and cooled in liquid air. Now about three hours' pumping brought the gauge reading down to 0.00002 mm. and $\lambda = 0.001226$. This is considered very fair agreement with that previously obtained, bearing in mind the smallness of the factor and the length of time required to get accurate results. At liquid air temperature there will be practically no gas given off from the metal, glass or cement so that the value obtained ($\lambda = 0.00123$) is probably a true

value of the internal friction of the wire. At room temperature this friction may be somewhat larger, but the increased value of λ is believed to be mainly due to vapor given off in the apparatus, of which the cement is the most probable source. As an approximation the effect was assumed proportional to the temperature but this approximation is not a serious one as will be seen when the method of applying the correction is shown. In fact whether the correction is put in as 0.0014 or 0.0012 will make a difference in the result of about 0.2% in the case of carbon dioxide at higher temperatures. For other cases the effect is smaller or larger according to whether the viscosity being determined is closer to or further from that of air at room temperature.

In the later form of apparatus there were no cements of any kind so that the only hindrance to obtaining high vacuum was the evolution of gas from the metal and glass. The procedure in this case was the same as before, pumping out being done after filling with hydrogen. Pumping for 36 hr. failed to give a constant value of the logarithmic decrement at room temperature so the apparatus was cooled in liquid air as before. This would effectually stop evolution of gas from the solid surfaces and ensure that the gas pressure was really low. Several hours further pumping brought the decrement to a steady value within experimental error. Three sets of readings spread over about $1\frac{1}{2}$ hr. gave the results 0.000758, 0.000703, 0.000731, which are in good agreement and give a mean of 0.000731. This value was accepted as reliable for the present work and is used in the calculation of all results obtained with the apparatus in the later form. In view of the fact that there were no materials present which would exert an appreciable vapor pressure at room temperature the one value of the correction was used for the whole range. The extension to the higher temperatures is justifiable as the results prove.

It will be noticed that the correction factor is only about 60% of that obtained previously with wire of the same size and kind. This reduction was obtained by annealing the wire *in situ* following the experience of Tomlinson (12) with other wire suspensions. The annealing was done at a relatively low temperature by passing steam through the jacket for several hours, but it seems to have had a good effect in the desired direction.

The way in which this single correction is applied is easily understood. The sample run given above was made with the later form of apparatus so the correction which applies is $x = 0.000731$. Now λ represents the effect of the gas and the wire so that due to the gas alone is $0.047373 - 0.000731$ or 0.046642. This is the decrement for one complete oscillation of time t, so that per second is $\frac{\lambda - x}{t}$. If the viscosity of the gas is η, then $\eta = \frac{\lambda - x}{Ct}$ where C is the constant of the apparatus. The run in this case was made with air and was for the purpose of determining the constant C. As previously mentioned, Millikan's values for the viscosity of air are used for this work in order that results should be comparable with those given in the International Critical Tables. At the temperature concerned (22.5° C.) air has a viscosity of 1820.2×10^{-7} whence the constant is calculated and comes out as $C = 5.0176$. Of course any changes in the apparatus change the value of the constant, and during some of the runs

with the later form the constant was inadvertently changed by the repeated cooling and warming. This worked the disks up a little at one side, so the adjusting tubes had to be opened and the screws fastened in place with DeKhotinsky cement. Fortunately this did not occur until after the wire correction was determined so that this remained unchanged. In any future work this difficulty can easily be overcome by altering the springs so that they do not hold the disks up, or by fastening a heavier piece to the disks so that they are always holding the screws down in their seats. After this experience of changing constant a check run at room temperature was made after every few runs to detect any variation. Such was not found to occur and so the calculation of all intermediate values can be made with confidence.

As an additional check on the constant and corrections of the apparatus, a series of experiments was carried out with hydrogen at room temperature. The viscosity of this gas has also been determined by Millikan's students with the same apparatus as used for air, so it may be taken as a reliable comparative value. Perfect agreement with this result was obtained with the present apparatus, which was gratifying as confirming the previous calibration as well as substantiating the value of the viscosity of hydrogen to some extent. For any future work of a similar kind it will be useful to have these accurate comparative figures on air and hydrogen. These gases form excellent calibrating materials since they are readily obtainable in a pure state and have such widely different viscosities. If there were any other correction which should be accounted for it would have been evident in the comparison with the two gases, but apparently those detailed above are all that are needed for the purpose.

Having completed the calibration of the apparatus the viscosities of the various gases were determined at the required temperature. Precisely as in the sample run, λ was determined from a series of readings. Knowing C and x, η is calculated from the formula.

At temperatures below the boiling point of the gas, reduced pressures must be used. It is well known that, over a wide range, the viscosity is independent of the pressure, so the results obtained are comparable with those in which atmospheric pressure was used. The validity of this conclusion, even at low temperatures, was confirmed by experiments over a wide pressure range. This apparatus was found to give the same values from 76 cm. down to about 2 cm. At 1 cm. pressure a slight falling-off is generally noticed. In view of this no experiments were carried out at less than 3 cm., which is safely over the limit required.

Results

The first part of the work was done with the apparatus in which the disks were held to the wall with cement. The results are shown in Table IV.

It was thought that the values in the literature for the viscosity of air at room temperature and at $-78.5°$ C. might be sufficiently dependable to allow of the calculation of the constant and correction of the apparatus. The equation as already given is $\eta = \frac{\lambda x}{Ct}$, so by substituting the two sets of values

TABLE IV

λ	t, sec.	T, °C.	λ	t, sec.	T, °C.
Air			Carbon dioxide		
.039487	47.56	12.6	.033026	47.54	21.8
.039480	47.52	12.7	.030658	47.54	1.3
.039519	47.56	12.8	.028442	47.52	−19.4
.028807	47.48	−78.5	.026139	47.49	−40.2
.028804	47.48	−78.5	.024116	47.50	−60.0
.028852	47.48	−78.5	.022174	47.48	−78.2
			.020535	47.50	−97.8

of η, λ, and t, one can solve for C and x. The value of η at the higher temperature was obtained by interpolation from the data in the International Critical Tables, namely, $\eta = 1772.3 \times 10^{-7}$ at 12.7° C. At −78.5° C. results by Vogel (15) and Schmitt (11) are available and give a mean of 1304×10^{-7} after correcting to refer to the same room temperature standard. With these figures, x comes out as an appreciable negative quantity which is impossible. Evidently the trouble lies with the assumed viscosity at −78.5° C. The difficulty was overcome by determining x directly by experiments at low pressure. These have already been explained and the results given. The values applying here are those varying from 0.00146 at 20° C. and 0.00123 at −183° C. Therefore the calculated constant for these experiments comes to be $C = 4.5144$. Using this, the viscosities are as shown in Table V.

TABLE V

VISCOSITIES OF AIR AND CARBON DIOXIDE

Gas	Temp, °C.	$\lambda - x$	$\eta \times 10^7$
Air	−78.5	.024747	1281.7
Carbon dioxide	21.8	.031565	1470.8
Carbon dioxide	1.3	.029212	1361.1
Carbon dioxide	−19.4	.027029	1259.9
Carbon dioxide	−40.2	.024750	1154.5
Carbon dioxide	−60.0	.022748	1060.8
Carbon dioxide	−78.2	.020825	971.6
Carbon dioxide	−97.8	.019208	895.8

With the later form of apparatus results were obtained with air and hydrogen at room temperature as well as the direct determination of the wire correction x. However, during the next experiments which were with carbon dioxide, slight movements of the disks occurred so that these were valueless. Obviously the wire correction is not affected by such changes so it applies throughout as 0.000731, but the constant C had to be redetermined for further work. The results for air on this occasion are those given earlier leading to $C = 5.0176$, and the only calculation in which this applies is that for hydrogen at 20.8° C. In this we have:

$\lambda = 0.023192$, $\lambda - x = 0.022461$, $t = 51.08$, whence

$\eta = 876.4 \times 10^{-7}$. This agrees well with Millikan's (9,10) value which by extrapolation to this temperature is about 877.6×10^{-7}.

As previously explained, the change in the constant of the apparatus was due to changes in temperature. That this is so is proved by the fact that, when

experiments immediately following one another were made on air and carbon dioxide at about the same temperature, good agreement with previous results was obtained as:-

Air at 20.8° C., $\lambda=0.049678$, $t=51.10$, gives $C=5.2861$.

Carbon dioxide at 21.8° C., $\lambda=0.040477$, $t=51.16$, with the above C, $\eta=1469.7\times10^{-7}$. This is plotted on the curve with other values and falls well into line. When the apparatus had been cooled in the interval, however, divergences of 5% or more were found.

TABLE VI

STANDARDIZATION OF APPARATUS WITH CARBON DIOXIDE (CONSTANT $C=4.5559$)

Temp., °C.	λ	t	$\eta\times10^7$
0.0	0.032307	51.09	1356.6
−65.6	0.024867	51.03	1035.6

After locating and remedying the trouble, the apparatus was again standardized, this time using carbon dioxide at room temperature. After experiments at lower temperatures, another standardization at room temperature was carried out. This agreed with that previously obtained within 0.1%. The results so obtained are shown in Table VI.

Some experiments were next carried out in liquid air and because, as was later found out, part of the tin foil coating had come off the apparatus and the ground connection was broken, no satisfactory readings could be obtained. Even when the bath full of liquid air was brought up round the apparatus with the greatest care, most violent movement of the swinging disk was caused, throwing the image completely off the scale. After allowing a long time for settling, the spot still had a movement of several centimetres and great discordance in results was obtained. Addition of more liquid air to the bath caused further violent movement and all the time the zero position kept changing over a range of several centimetres. When the liquid air was removed and the apparatus allowed to warm up to room temperature, further violent oscillations were observed but finally the image settled to a steady position on the scale not more than 1 mm. from the previous position of rest at room temperature. At this temperature, with the apparatus filled with air, a set of experiments was carried out giving results that checked closely with the preceding ones on carbon dioxide, showing that the procedure just described had not affected the working of the apparatus at room temperature.

However, in order that it might be possible to do the low temperature work, the apparatus was thoroughly cleaned off and the whole of the lower part covered with tin foil which was earthed. Unfortunately in this work it was impossible to avoid slight disturbance to the apparatus so it was necessary to reset it and to make a further standardization. This was done with air at room temperature as usual and gave the result $C=4.5900$. This treatment was found to be entirely effective in preventing the disturbances before observed with liquid air, thus showing fairly conclusively that electrostatic charges were responsible.

All the rest of the experiments described herein were completed without altering the constants of the apparatus again. This is proved by the fact that experiments with hydrogen at room temperature, and also with carbon dioxide at various temperatures, gave results agreeing with those previously determined. The results are collected and arranged in Table VII. Generally the value of λ given is the mean of two distinct sets of readings each involving the measurement of at least ten complete oscillations. In a few cases it is the mean of three or more such sets. As previously mentioned, slight temperature changes occur during some of the runs so of course the value of λ will change also. This was always small, however, and the results may be averaged, since they are practically proportional to the temperature. Experimental errors never gave rise to variations exceeding 0.4% and usually were considerably less. The values of η have a small correction applied to them to allow for the contraction of the disks at the lower temperatures. This is proportional to the temperature to a sufficiently close approximation and is of the order of 0.1% at $-70°$ C.

TABLE VII

RESULTS OBTAINED WITH AIR, HYDROGEN AND CARBON DIOXIDE

Gas	T, °C.	t	P	λ	$\lambda-x$	$\eta\times10^7$
Air	20.8	51.09	1 atm.	0.043214	0.042483	1811.6
Air	0.0	51.07	1 atm.	.040776	.040045	1708.3
Air	−31.6	51.08	1 atm.	.036791	.036060	1539.2
Air	−69.4	51.04	1 atm.	.031908	.031177	1332.8
Air	−104.0	51.01	1 atm.	.027124	.026393	1129.5
Air	−183.1	50.85	1 atm.	.015314	.014583	626.9
Air	−194.2	50.92	8 cm.	.013562	.012831	551.1
Hydrogen	20.7	51.11	1 atm.	.021291	.020560	876.4
Hydrogen	0.0	51.07	1 atm.	.020307	.019576	835.1
Hydrogen	−31.6	51.08	1 atm.	.018695	.017964	766.9
Hydrogen	−62.6	51.02	1 atm.	.017108	.016377	700.6
Hydrogen	−97.5	50.97	1 atm.	.015075	.014344	615.2
Hydrogen	112.6	50.98	1 atm.	.014205	.013474	576.9
Hydrogen	−113.5	50.98	1 atm.	.014074	.013343	571.5
Hydrogen	−123.7	50.95	1 atm.	.013507	.012776	547.5
Hydrogen	−183.4	50.91	1 atm.	.009776	.009045	388.4
Hydrogen	−195.2	50.92	1 atm.	.008775	.008044	345.4
Hydrogen	−198.4	50.93	1 atm.	.008558	.007827	336.0
Carbon dioxide	−35.0	51.04	1 atm.	.028485	.027754	1184.7
Carbon dioxide	−73.7	50.99	1 atm.	.024191	.023460	1002.4
Carbon dioxide	−95.4	50.98	3 cm.	.021931	.021200	906.0

The first of these values for air is the standard from which the constant is calculated. It is $C=4.5900$. From this all the other values were determined.

The relation between viscosity and temperature for each of the three gases is clearly shown by the accompanying curves (Fig. 2). It will be seen that at the higher temperatures the relation is nearly a straight-line function but curvature is shown as the temperature falls. It is interesting to note that in the case of carbon dioxide the slope decreases, whereas the reverse is true in the cases of air and hydrogen. In comparing the curves it should be remem-

bered that the values for carbon dioxide are all below the critical temperature (31.1° C.), and for hydrogen they are all above (−234.5° C.), while air is intermediate, its critical temperature being about −140° C.

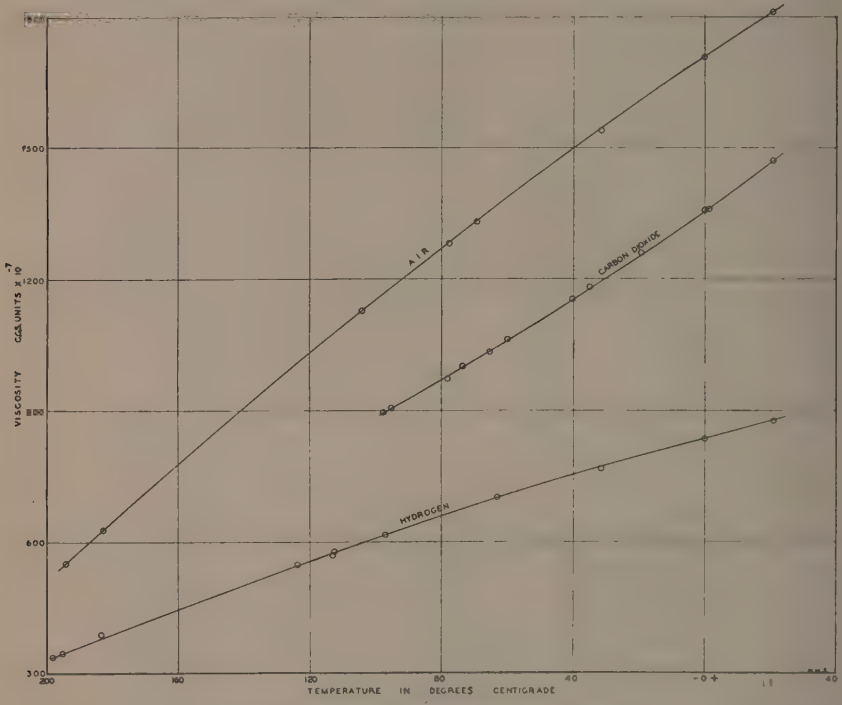

FIG. 2. *Variation of viscosity with the temperature.*

The accepted values for carbon dioxide given in the International Critical Tables are too high at the lower temperatures. At room temperature there is good agreement with the values of Vogel (15), Van Dyke (14), Ishida (3), and Trautz and Kurz (13).

For air the only points of comparison available from the International Critical Tables are at and above 0° C. and as the values at higher temperatures were used for calibration the one point left to compare is at 0° C. Here agreement is to within 0.1%, which is excellent.

In the case of hydrogen the values in the I.C.T. are more conflicting. However it is believed that the value obtained by Millikan's students is at least as reliable as any other and with this the present results are in agreement to about 0.1%. At the lowest temperatures again, close agreement with the values in the I.C.T. is shown although at intermediate points the present results tend to be somewhat smaller than those given previously. However, this is by no means a proof of inaccuracy, as the literature will also give results in conformity with the present ones if care were taken to select them from the mass of data.

Actual figures on one other point should be given, *i.e.*, on the relation between viscosity and pressure at low temperatures. It was found that in each case the logarithmic decrement began to fall off at about 1 cm. as previously mentioned. This was doubtless due to the "slip" effect, the viscosity itself being constant. In any event viscosity as measured by this apparatus is constant down to 2 cm. The results are given in Table VIII.

So from this point of view these gases behave the same way at low temperatures as they do at higher ones.

TABLE VIII

RELATION BETWEEN VISCOSITY AND PRESSURE AT LOW TEMPERATURES

Gas	Temp., °C.	Pressure	λ
Air	−183.1	1 atm.	.015314
Air	−183.0	30 mm.	.015363
Air	−183.0	20 mm.	.015348
Air	−183.0	10 mm.	.015403
Hydrogen	−183.0	1 atm.	.009776
Hydrogen	−183.0	10 mm.	.009753
Carbon dioxide	− 78.5	400 mm.	.025095
Carbon dioxide	−78.5	10 mm.	.024917

In conclusion it may be stated that, for the work as a whole, it is claimed that with one and the same apparatus a complete set of concordant results has been obtained covering a wide temperature range, so that it may be safely concluded that the shape of the viscosity-temperature curves is that shown in the diagram. The analysis of these results from the point of view of information of theoretical interest will be considered in a subsequent paper.

The claim is made that the data given are of a greater accuracy than any available, except those at room temperature, and for this reason the improvement in the apparatus and the detail of the experimental procedure has been given very fully in order to substantiate this claim.

An extensive programme involving the investigation of other gases is now under way.

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A PHOTO-ELECTRIC CELL CIRCUIT[1]

By G. A. Woonton[2] and R. G. Elson[3]

Abstract

In this paper it is shown that a vacuum tube circuit of special design is capable of linear response to the varying conductivity of a photo-electric cell. A method is suggested whereby light intensities of widely different magnitudes can be compared. The circuit is shown to be extremely stable.

Fig. 1 is the diagrammatic representation of a circuit developed by Hull (4) for use where fluctuations in light intensity are to be reproduced electrically by means of a photo-electric cell. For the present purpose it has been re-adapted to give quantitative measurement of the amount of ultra-violet light in sunshine and skyshine, and to determine the ultra-violet reflecting and transmitting properties of various materials. The same circuit may be used as a densitometer for the measurement of film densities or, with a very slight change, as a resistance meter for the measurement of the variation in the resistance of crystals and salts where the resistances involved are of a large order of magnitude.

Circuit Theory

It is obviously impossible to calibrate the circuit by illuminating the cell and measuring the input and output currents over a range of light intensities. The investigation of the nature of the amplification can be made only on a theoretical basis.

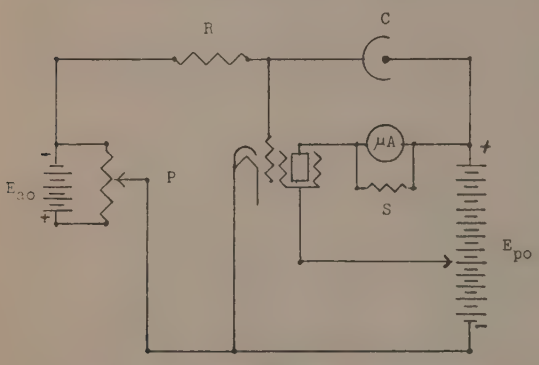

Fig. 1. *The original circuit. μA, Micro-ammeter; C, photo-electric cell; E_{ao}, "A" grid bias battery; E_{po}, plate battery; P, potential divider; R, high resistance; S, shunt; tube, UY-224.*

Referring to Fig. 1—if the resistance of the photo-electric cell is altered by a change in the energy falling on the cell, the current flowing in the outer circuit C, R, E_{ao}, E_{po} is altered and the potential drop across R changes. An increase in current flowing through R, because of the polarity of the batteries, must be such that the end of R next to the control grid becomes more positive with respect to the other end. E_{ao}, the potential due to the biasing battery, gives the control grid a constant negative bias with respect to the cathode. The effective bias of the control

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grid must therefore be made up of two parts—a constant bias E_{ao} and a varying bias in the opposite direction due to the current flowing through the high resistance R. The current flowing in the output circuit, according to the usual theory, is a function of this bias.

For the purpose of this analysis it should be noted that it is necessary to define the resistance of the photo-electric cell C, as the reciprocal of the conductivity of the cell at constant anode voltage but with varying light flux. This is contrary to usual practice. C in this case is a variable even though the ratio $\frac{\text{anode voltage}}{\text{anode current}}$ is a constant for constant light flux.

The type of mathematical analysis used in determining the form of the function is that developed by Carson (2), Llewellyn (5) and Brainerd (1).

Let E represent a potential difference and I a current. Let the subscripts p, a and b refer to the plate, control-grid and screen-grid circuits respectively. Further, let the subscript o indicate a steady condition and the lower case letters e or i indicate a variation around such a steady value.

We may write for the various circuits

$$\begin{aligned} E_p &= E_{po} + e_p & I_p &= I_{po} + i_p \\ E_a &= E_{ao} + e_a & I_a &= I_{ao} + i_a \\ E_b &= E_{bo} + e_b & I_b &= I_{bo} + i_b \end{aligned} \tag{1}$$

The following functional relations are quite general:—

$$\begin{aligned} I_p &= I_p(E_a, E_b, E_p) \\ I_a &= I_a(E_a, E_b, E_p) \end{aligned} \tag{2}$$

If $e_a = e_b = e_p = 0$, the plate current must be in its normal steady state and $i_p = 0$. Then

$$I_{po} = I_p(E_{ao}, E_{bo}, E_{po})$$

From Equation (1)

$$i_p = I_p - I_{po}$$

therefore

$$i_p = I_p(E_a, E_b, E_p) - I_p(E_{ao}, E_{bo}, E_{po})$$

and similarly

$$\begin{aligned} i_a &= I_a(E_a, E_b, E_p) - I_a(E_{ao}, E_{bo}, E_{po}) \\ i_b &= I_b(E_a, E_b, E_p) - I_b(E_{ao}, E_{bo}, E_{po}) \end{aligned} \tag{3}$$

Each of these relations may be developed into a Taylor's series evaluated in the neighborhood of the steady values.

$$i_p = \frac{\partial I_p}{\partial E_a} e_a + \frac{\partial I_p}{\partial E_b} e_b + \frac{\partial I_p}{\partial E_p} e_p + \tfrac{1}{2} \frac{\partial^2 I_p}{\partial E_a^2} e_a^2 + \tfrac{1}{2} \frac{\partial^2 I_p}{\partial E_b^2} e_b^2 + \ldots, \tag{4}$$

which may be written for convenience,

$$i_p = P_1 e_a + P_2 e_b + P_3 e_p + P_4 e_a^2 + P_5 e_b^2 + P_6 e_p^2 + \text{etc.}, \tag{5}$$

and similarly

$$i_a = A_1 e_a + A_2 e_b + A_3 e_p + A_4 e_a^2 + A_5 e_b^2 + \text{etc.}$$

Since the resistance of the output meter and its accompanying shunt is insignificant E_p must be constant. Therefore $E_p = E_{po}$ and $e_p = 0$; by similar reasoning

$$e_b = 0$$

whence

$$i_p = P_1 e_a + P_4 e_a^2 + \text{etc.},$$
$$i_a = A_1 e_a + A_4 e_a^2 + \text{etc.} \tag{6}$$

In the a grid circuit R may be thought of as a source of e.m.f., due to the drop in potential across it when a current flows in the circuit C, R, E_{ao}, E_{po}. If the potential difference due to this cause be defined as e, we have

$$e \equiv \frac{E_{ao}+E_{po}}{R+C} R = \frac{VR}{R+C}, \tag{7}$$

if $P \ll R$, where P is resistance of potential divider, C is the resistance of the photo-electric cell, and V is the effective potential applied to the cell circuit.

If the value of C decreases, the grid becomes more positive relative to the cathode. The balance between secondary and primary emission from and to the grid is disturbed by the change in potential, and I_a varies slightly. The variation i_a in the grid current causes a drop in potential across R in the opposite direction to that caused by the current in the outer circuit; the value of the change in the potential drop must be $i_a R$. The net change in the potential of the grid with respect to the cathode may be written

$$e_a = e - i_a R \tag{8}$$

We may express i_a as a formal power series in terms of e

$$i_a = b_1 e + b_2 e^2 + \ldots\ldots\ldots + , \tag{9}$$

where the b's are undetermined coefficients.

Substituting in Equation 8

$$e_a = e - (b_1 e + b_2 e^2 + \ldots\ldots\ldots)R$$
$$= (1 - b_1 R)e - b_2 R e^2 + \ldots\ldots\ldots + \tag{10}$$

Substituting (9) and (10) in (6)

$$b_1 e + b_2 e^2 + \ldots\ldots\ldots + = A_1[(1-b_1 R)e - b_2 R e^2 + \ldots\ldots +]$$
$$+ A_4[(1-b_1 R)e - b_2 R e^2 + \ldots\ldots + \ldots]^2 \tag{11}$$

From which b_1 and b_2 may be evaluated by equating like powers of e,

$$b_1 = \frac{A_1}{1+A_1 R} \qquad b_2 = \frac{A_4}{(1+A_1 R)^3}. \tag{12}$$

Therefore

$$e_a = (1 - \frac{A_1 R}{1+A_1 R})\, e - \frac{A_4 R e^2}{(1+A_1 R)^3} + \ldots\ldots\ldots + \ldots\ldots$$

$$= \frac{e}{(1+A_1 R)^3}[(1+A_1 R)^2 - A_4 R e + \ldots\ldots +]. \tag{13}$$

But according to Equation (6)

$$i_p = P_1 e_a + P_4 e_a^2 + \ldots\ldots\ldots\ldots + .$$

Therefore we may write

$$i_p = \frac{P_1 e}{(1+A_1 R)^3}[(1+A_1 R)^2 - A_4 R e + \ldots\ldots + \ldots\ldots +]$$

$$+ \frac{P_4 e^2}{(1+A_1 R)^6}[(1+A_1 R)^2 - A_4 R e + \ldots\ldots]^2 + \ldots\ldots\ldots + \tag{14}$$

By definition

$$\mu_a = \frac{\dfrac{\partial I_p}{\partial E_a}}{\dfrac{\partial I_p}{\partial E_p}} \qquad \mu_b = \frac{\dfrac{\partial I_p}{\partial E_b}}{\dfrac{\partial I_p}{\partial E_p}}$$

$$\frac{1}{r_p} = \frac{\partial I_p}{\partial E_p} \qquad g_a = \frac{\mu_a}{r_p} = \frac{\partial I_p}{\partial E_a} \tag{15}$$

$$g_b = \frac{\mu_b}{r_p} = \frac{\partial I_p}{\partial E_b}$$

$$\frac{1}{r_{ga}} = \frac{\partial I_a}{\partial E_a} \qquad \frac{1}{r_{gb}} = \frac{\partial I_p}{\partial E_b}$$

The P's and A's may be expressed in terms of these definitions

$$P_1 = \frac{\partial I_p}{\partial E_a} = g_a \qquad A_1 = \frac{\partial I_a}{\partial E_a} = \frac{1}{r_{ga}} \tag{16}$$

$$P_4 = \tfrac{1}{2}\frac{\partial^2 I_p}{\partial E_a^2} = \tfrac{1}{2}\frac{\partial g_a}{\partial E_a} \qquad A_4 = \tfrac{1}{2}\frac{\partial^2 I_a}{\partial E_a^2} = \frac{1}{2r_{ga}^2}\frac{\partial r_{ga}}{\partial E_a}$$

Substituting in (14) from (16)

$$i_p = \frac{g_a r_{ga}^3}{(R+r_{ga})^3} e \left\{ \left(\frac{r_{ga}+R}{r_{ga}} \right)^2 - \frac{1}{2r_{ga}^2}\frac{\partial r_{ga}}{\partial E_a} Re + \dots \right\}$$

$$+ \tfrac{1}{2}\frac{\partial g_a}{\partial E_a}\frac{r_{ga}^6}{(R+r_{ga})^6} e^2 \left\{ \left(\frac{r_{ga}+R}{r_{ga}} \right)^2 - \frac{1}{2r_{ga}^2}\frac{\partial r_{ga}}{\partial E_a} Re + \dots \right\}^2 + \dots + \dots \tag{17}$$

If the range over which the mutual conductance g_a is constant is chosen as the working range of the tube, then Equation (17) reduces to

$$i_p = \frac{g_a r_{ga}^3}{(R+r_{ga})^3} e \left\{ \left(\frac{r_{ga}+R}{r_{ga}} \right)^2 - \frac{1}{2r_{ga}^2}\frac{\partial r_{ga}}{\partial E_a} Re + \dots \dots + \right\}. \tag{18}$$

By definition $r_{ga} = \dfrac{\partial E_a}{\partial I_a}$ *i.e.*, the reciprocal of the slope of the a grid current$-a$ grid bias curve. If the working range of the tube is further restricted to include only that range of biases for which this slope is constant, then

$$\frac{\partial r_{ga}}{\partial E_a} = 0,$$

and Equation (18) reduces to

$$i_p = \frac{g_a r_{ga}}{R+r_{ga}} e, \tag{19}$$

or, substituting the value of e from Equation (7),

$$i_p = \frac{g_a r_{ga}}{R+r_{ga}} \frac{E_{ao}+E_{po}}{R+C} R. \tag{20}$$

If C is kept very much larger than R, Equation (20) may be written in the approximate form

$$i_p \doteq \frac{I}{C} \frac{g_a r_{ga}}{R+r_{ga}} (E_{ao}+E_{po}) R. \tag{21}$$

In this equation i_p varies inversely as the resistance of the photo-electric cell, all the other terms having been made constants. Grouping the various constants

$$i_p = \frac{K'}{C} \tag{22}$$

If the photo-electric cell has such characteristics that its resistance varies inversely as the energy falling on it, then

$$L = \frac{K''}{C} \tag{23}$$

where L is the light intensity.
Substituting (23) in (22)

$$i_p = KL \tag{24}$$

That is to say that if the assumptions leading up to this equation can be fulfilled then the circuit is capable of linear amplification.

Eight assumptions were made in obtaining the result given by (24). These were— (i) The circuit theory given at the beginning of this section; (ii) The functions given by Equation (2); (iii) $e_p = e_b = 0$; (iv) Terms of the various series higher than the second are negligible; (v) The mutual conductance of the tube over the working range is constant; (vi) r_{ga} is constant over the working range; (vii) C, the resistance of the cell, is very much larger than R the resistance of the grid circuit; (viii) The resistance of the photo-electric cell varies inversely as the light intensity.

Assumptions (i) and (ii) are based upon generally accepted vacuum tube theory.

Assumption (iii) is realized in practice. The screen grid battery is connected directly across the tube elements. If a sufficiently sensitive output meter is used in the plate circuit the shunt across it need not exceed five ohms. The drop in potential across a resistance of this order, with currents of the magnitude passed by a UY-224 tube, is inappreciable.

Assumption (iv) can be shown to be justified by the rapid convergence of the various series involved, but it is easier to prove the soundness of the assumption through the medium of assumption (v). Equation (17) is the expression into which the various series are combined. The two terms shown are not approximations; all possible terms are included in them. Further expansion of the various series shows that every term of Equation (17) higher than the first contains as a multiplier a derivative of the mutual conductance of some order. If the mutual conductance is to remain constant over the working range then each of these terms vanishes and we are justified in dropping terms, of all series, higher than the second.

Assumption (v) is justified by choosing for the working range of the tube that interval over which the mutual conductance is constant.

Assumption (vi) is that r_{ga} is constant over the working range. This assumption may be shown to be true by experimental measurement.

The resistance of the photo-electric cell was measured under the condition of greatest possible illumination and found to be in excess of 100 megohms.

The value of R used in measuring light of similar intensity was one megohm. In this case the error due to this cause is less than the error in meter reading. The assumption imposes a limit on the amplification which can be obtained in practice.

The cell used in this circuit was of the vacuum type and gave resistance variations proportional to the variations in light intensities.

Equation (24) indicates that only the variation in plate current is important. A bucking battery was added to the circuit to balance out the normal plate current through the output meter and thus allow greater accuracy in reading. The zero light intensity was chosen as that when the photo-electric cell shutter was closed. The bucking battery was adjusted to reduce the output meter reading to zero for this value of light intensity.

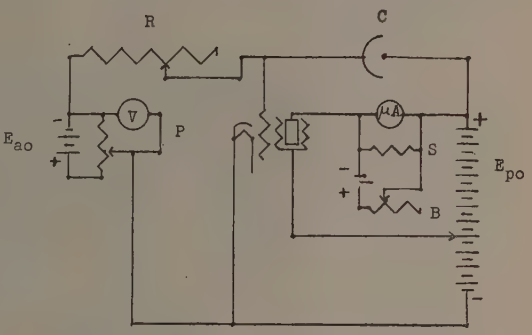

FIG. 2. *Circuit revised to allow more flexible measurements. μA, C, E_{ao}, E_{po}, P, R, S, tube,—as in Fig. 1; B, bucking battery and series resistance; V, voltmeter.*

Fig. 2 is a diagram of the circuit modified to conform with the limitations of the previous paragraphs.

It can be shown that if the negative grid bias of a UY-224 tube exceeds a critical bias of about 1.5 volts, the value of r_{ga} is approximately equal to 15,000 megohms. Since this is very large compared to the highest value of R used, Equation (21) may be still further reduced to

$$i_p = \frac{1}{C} g_a R(E_{ao}+E_{po})$$

or

$$C = \frac{1}{i_p} g_a R(E_{ao}+E_{po}). \qquad (25)$$

For each value of R a graph in the form of an equilateral hyperbola may be drawn between C and i_p. The resistance of the photo-electric cell may be taken as an arbitrary unit of light intensity and hence light intensities may be compared regardless of the value of R in the circuit.

The theoretical upper limit of amplification cannot be obtained in practice because of the various limitations imposed in the previous paragraphs. Any of the factors grouped under K' in Equation (22) may be increased to obtain higher amplification. Of these factors R may be most easily controlled. The theoretical upper limit of R can be determined as follows—

$$i_p = \frac{g_a r_{ga}}{R+r_{ga}} \cdot \frac{E_{ao}+E_{po}}{R+C} R, \tag{20}$$

$$\frac{\partial i_p}{\partial R} = \frac{g_a r_{ga}(E_{ao}+E_{po})\,(Cr_{ga}-R^2)}{(R+r_{ga})^2\,(R+C)^2}.$$

The change in plate current with varying values of R for any given value of C is maximum when

$$\frac{\partial i_p}{\partial R} = 0,$$

i.e., when $R=\sqrt{Cr_{ga}}$.

For most tubes and photo-electric cells the product Cr_{ga} is so large that the maximum value of R will not be reached in practice. The only limit that need be imposed on R therefore is that made necessary by assumption (vii).

The chief advantage of the screen-grid tube in this circuit lies in its stability. Other tubes of higher mutual conductance might be chosen, but all of these, with the possible exception of the space charge pentode, have characteristics which render them inferior to the screen grid tube in the matter of stability.

It can be shown that the UY-224 tube used in a screen grid circuit has an exceptionally high plate impedance. For this reason the plate current is practically independent of the plate potential, provided that the plate potential does not fall from its rated value of 180 volts to within more than 15 volts of the screen potential. It is evident that no attempt need be made to stabilize the plate battery.

Measurement shows that the plate current-screen grid potential curves are all parallel to one another over a wide range of grid bias. Since, in practice, variations in plate current only are of interest, if the mutual conductance of the tube remains constant, the total values of the plate current from which the variation is calculated are not of importance. The parallelism of the various curves indicates that changes in screen potential cause a change in the total value of the plate current without changing the mutual conductance over the range defined by the linear portion of the curve. Stabilization of the screen battery is unnecessary for this circuit.

If the circuit is used in measuring light intensities where the highest possible amplification is necessary, the filament current source should be a high capacity storage battery stabilized by the method suggested by Dearle and Matheson (3). For ordinary measurements where the greatest sensitivity is not necessary the tube may be heated by means of alternating current. The sensitivity of the circuit is increased to a value slightly higher than would ordinarily be necessary, and the sensitivity of the output meter decreased by decreasing the shunt across it.

Since the error due to variations in filament current is independent of the sensitivity of the circuit, the percentage error due to this cause is decreased by this method. In all cases better operation has been obtained by allowing the tube to heat for 30 or 40 min. before attempting to take readings.

While fair results have been obtained with the circuit in an unshielded case, shielding has been found to give much greater stability. Shielding is absolutely necessary if the circuit is to be used in measuring light intensities such that the ultimate sensitivity is required. It has been found that better results are obtained if the shield and the positive end of the *B* batteries are grounded.

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